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KINETIC METHODS OF QUANTITATIVE ANALYSIS

1. THE THEORETICAL BASES OF KINETIC METHODS OF QUANTITATIVE ANALYSIS

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The rate of a chemical reaction in solution is determined by the concentration of reactants, and, in certain cases, by catalyst concentration. When there is a relation between reaction rate and concentration, it can be used for quantitative determinations.

Catalysis is fairly widely used in qualitative analysis for the detection of small amounts of many metals. Numerous investigations carried out by various authors have not only demonstrated the possibility of using this method, but have also established its advantages with respect to selectivity (in certain cases even with respect to specificity) and high sensitivity. Thus, Krumholz and Watzek [1], established that negligible amounts of gold (of the order of 10^{-11} g) can be detected by its catalytic effect on the reaction between silver salts and divalent iron. Shilov and Kupinskaya [2], found that copper at concentrations of the order of 10^{-9} mol/liter essentially affects the decomposition rate of H_2O_2 in alkaline media.

The number of papers devoted to the application of kinetic methods in quantitative analysis is appreciably smaller. Nikitin [3], developed a so called " chronometric method of analysis", based on the use of the relation between the length of the induction period and reactant concentration; in conjunction with coworkers he worked out a number of applications of this method; Ponomareva [4], extended the scope of the chronometric method and suggested its use for the determination of several inorganic compounds.

Work on so called "catalytic analysis" has received particular attention in recent years. Papers by the Japanese research workers Goto, Sudo, Shiokuwa, Suzuki, et al, have been devoted to this question [5-8]. Their work was preceded by that of Hahn and Limbach [9], Sinyakova [10], Sandell and Kolthoff [11], Gleu [12], et al.

It is impossible to give a complete review of the numerous papers devoted to catalytic methods within the framework of this article.

Despite the comparatively large number of papers on the application of kinetic methods in quantitative analysis, a complete theoretical analysis of the question has not been made. The absence of an analysis of the theoreti-

cal basis of these methods however hinders their further development. Let us therefore consider the most important conditions which determine the possibility of using kinetic methods, and the scope of their application.

One of the basic conditions for the successful application of kinetic methods is maintenance of the concentration of the element to be determined at an approximately constant value during measurement. During the reaction, the amount of test material which is used up while measurements are made should not exceed 5% of its initial content. This condition is observed if the initial concentration of test material is comparatively high, or if it is used as a catalyst, or if, finally, a characteristic "buffering" occurs when making use of complex formation. Thus, Fe^{3+} concentration can be made relatively constant by adding excess sulfate to the solution. By keeping the ratio of $FeSO_4^+$ concentration to SO^{2-} concentration approximately constant, (most of the iron will be found in the form of this complex) the concentration of Fe^{3+} will also be approximately constant.

Of essential significance also is the choice of the time of observation – i.e., the time during which the rate of a given reaction is measured. If the time interval is too long, then this method will lose one of its most important advantages – viz. the speed with which it can be carried out. If, on the other hand, the time interval is too short, it will be impossible to make accurate measurements, or to determine the indices characterizing the rate of reaction accurately (e.g., measurements of optical density). We reckon that the optimum time interval is 5-15 minutes. The reactants should also be present at optimum concentrations, so that, during the 5-15 minutes, the property being measured should change appreciably (optical density e.g. should change by a few dozen percent).

The most important condition for the successful application of kinetic methods of quantitative analysis is maintenance of the same values for reaction rate constants (or catalytic coefficient) when drawing up a calibration curve, (or compiling a set of equations) and during measurement of the concentration of reactants in the test material. In this connection, it is necessary to take into account all the factors which affect the reaction velocity constants; temperature variations, presence of contaminants, and ionic strength of the solution. For quantitative kinetic determination it is essential to choose reactions with low temperature coefficients, and to carry out determinations at temperatures which are as near as possible; thermostating would complicate the method considerably. Before carrying out any determinations it is necessary to elucidate as much as possible the influence of background, and to construct a calibration curve under conditions which approximate as closely as possible to test conditions.

Let us consider two basic examples of the determination of the concentration of materials by means of kinetic methods.

The relation between the rate of a chemical reaction and reactant concentration is expressed by the equation:

$$v = kc_A^n c_B^m, \qquad (1)$$

where v is the reaction velocity; k – a constant; n and m – usually whole numbers; c_A and c_B – the concentrations of the reactants.

If the concentrations of all the reactants remain practically constant during the course of the experiment, then the reaction velocity will also remain constant. This state of affairs is true e.g. in the reaction between

hydrogen peroxide and iodine. When small amounts of the reactants are used up, small amounts of iodine are also liberated which are sufficient for detection by sensitive methods, and consequently can be used for fairly accurate determination of reaction velocity. Reaction rate is determined by the change in concentration of the material formed in unit time. For this purpose it is best to construct a graph of time-concentration and to determine the slopes of the straight lines formed. Thus, if the concentration of a material B is known (or it is known that its concentration remains constant):

$$c_A = \frac{1}{\sqrt[n]{kc_B^m}} \sqrt[n]{v} \tag{2}$$

or

$$c_A = k' \sqrt[n]{v} \tag{2a}$$

where k' is an arbitrary constant. In the special case where n = 1

$$c_A = k'v. \tag{2b}$$

The concentration of material A can be determined by means of equation 2a or from the graph of $c_A - v^{1/n}$ constructed beforehand.

If, during the time interval selected, the concentration of one of the reactants changes appreciably, then the method described will not be applicable, since the reaction rate does not remain constant. In such cases kinetic equations in an integral form can be used.

Let us consider the simplest case, in which the concentration of material, by means of which reaction rate is determined, is only raised to the first power in the kinetic equation:

$$-\frac{dx}{dt} = kc_A^n x. \tag{3}$$

Here x denotes the concentration of B (in accordance with the conditions formulated above, for kinetic determinations $x \ll c_A$). After integration of equation (3) and substituting natural logarithms by logarithms to the base ten, we get:

$$\log a - \log x = kc_A^n t, \tag{4}$$

where a is the initial concentration of B, and t is the time.

The concentration of A can be found by determining the time necessary for the reaction to proceed half way (x = a/2), when:

$$kc_A^n t_{1/2} = \log 2 \tag{5}$$

$$c_A^n = \frac{k''}{t_{1/2}}, \tag{5a}$$

where k is a constant.

The concentration of A can be found from equation (5a) or by means of a graph constructed beforehand of $c_A - \frac{1}{\sqrt[n]{t_{1/2}}}$ on the basis of measurements of $t_{1/2}$ for several values of c_A.

Equation (3) is applicable to many catalytic reactions (in this case, k is the catalytic coefficient, while c_A is the catalyst concentration). Consequently the examples considered here can also be applied for determination of concentrations during "catalytic analysis". Actually, the Japanese workers mentioned above [5-8], widely used the method of determining catalyst concentration on the basis of measurements of the time taken for the reaction to get to the half-way stage. It would be possible of course to determine the concentration of reactants by measuring any other definite time interval (the time taken for the reaction to proceed $^1/_2$, $^1/_3$ of the way, etc.).

If a graph of log x-t is constructed (some other factor, e.g., the optical density, which is proportional to x, can be used instead of x), and the slopes of the corresponding straight line determined, then from equation (4) it follows that

$$y = kc_A^n, \tag{6}$$

where y is the absolute value of the slope. Concentration c_A can be found either from equation (6), or from the graph of $c_A - \sqrt[n]{y}$. A graph of this type can also be constructed by means of values of c_A and y found beforehand.

If the concentration of B is raised to the second power in the kinetic equation, then other relations are obtained: the time taken for the reaction to go half-way depends on the initial concentration of B, no linear relation is observed between log x and time. It is very important therefore, when kinetic methods are used, that the kinetic equation of the reaction being studied be known. In the absence of such information, serious errors are possible, if the methods considered above for the determination of concentrations are used automatically as a basis. The methods discussed above only apply to the special cases considered.

For the determination of the concentration of any material on the basis of a study of its catalytic effect ("catalytic analysis") one should bear in mind that two parallel reactions occur in solution, the normal reaction and the catalytic reaction, each at different rates:

$$v = kc_A^n c_B^m ; \tag{7}$$

$$v_c = \kappa c_c c_A^n c_B^m \tag{7a}$$

where v and v_c are the reaction rates of the normal and catalytic reactions respectively; k – the velocity constant of the reaction; κ – the catalytic coefficient; c_c – catalyst concentration.

In order to measure the rate of the catalytic reaction, it is necessary that it should amount to at least 10% of the normal reaction rate, since the accuracy of velocity determinations, in the methods described, will hardly exceed $\pm 5\%$, and at lower values of v_c its magnitude will lie within the limits of experimental error, then

$$\frac{v_c}{v_1} = \frac{\kappa c_c}{k_1} \geq 0.1 \tag{8}$$

and consequently,

$$c_{c_{min}} \quad 0.1 \frac{k_1}{\kappa} .$$

Accordingly, the minimum concentration of material K, which can be analyzed by means of catalytic analysis, depends on the ratio of the respective constants.

It is possible to determine by means of kinetic methods of analysis, not only concentrations of reactants, but also the concentration of materials which can interact with the reactants. Materials which interact with the reactants or catalysts slow down the reaction, and it is possible to estimate the amount of such materials present by the extent of the slowing down produced by them. These indirect determinations could be called "reverse, or back" kinetic determinations, by analogy with back titration.

Kinetic methods of quantitative analysis have a number of positive advantages; the possibility of determining extremely small amounts of material (amounts which are completely outside the scope of other methods), speed of determination, possibility of determining equilibrium concentrations, and finally, in some cases, exceptional specificity. The drawbacks of these methods include comparatively large experimental errors, the possibility of the presence of factors which it is difficult to take into account but which have a considerable effect on reaction velocity, and the absence of any general method.

SUMMARY

Conditions under which kinetic methods of quantitative determinations are applicable have been considered, as well as methods of determining concentrations of materials on the basis of kinetic results. It has been shown that the minimum concentration of a test element which can be determined by catalytic analysis depends on the ratio of the velocity constants of the reactions and the catalytic coefficient.

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KINETIC METHODS OF QUANTITATIVE ANALYSIS

2. DETERMINATION OF THIOSULFATE AND COPPER

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Oxidation of thiosulfate by ferric ions proceeds at a measureable velocity.

Tetrathionate is formed on oxidation of thiosulfate:

$$2Fe^{3+} + 2S_2O_3^{2-} = 2Fe^{2+} + S_4O_6^{2-}. \qquad (I)$$

Reaction rate increases rapidly in the presence of small amounts of copper salts, which catalyze this reaction.

Holluta and Martini [1] studied the reaction kinetics of (I) at comparatively high concentrations of reactants and acid. The catalytic effect of copper salts on this reaction is used for the detection and quantitative determination of copper [2-4].

We decided to investigate the possibility of using reaction (I) for determining thiosulfate concentration, and also to find ways of increasing the accuracy of copper determinations on the basis of its catalytic effect, and to establish the application limits of this method.

EXPERIMENTAL

To determine the reaction rate of (I), $FeCl_3$, $Na_2S_2O_3$, and KCNS were introduced into solution and a FM-photometer used for determining optical density after definite time intervals.

The following solutions were used, $FeCl_3$ (acidified with HCl) – 0.00233 M, KCNS – 0.242 M, $Na_2S_2O_3$ – 0.00400 M, all prepared from chemically pure materials. 5 ml of $FeCl_3$ solution, 10 ml of KCNS, and variable amounts of $Na_2S_2O_3$ solution were introduced into a 50 ml flask. Water was then added to bring the volume up to the mark, the solution carefully mixed and introduced into a photometer cell (HCl concentration after dilution 0.0033 M). A stopwatch was started off at the same time as the first measurement of optical density was made, further measurements of optical density were then made after equal time intervals (1, 2, or 3 minutes). The experiment was terminated when the reaction had gone half way (halving of the optical density). A calibration curve was then constructed of time – logarithm of the optical density. Optical density was determined at an effective wave length of 496 mμ; all experiments were made at 14-15° (Fig. 1).

The same solutions were used for the determination of equilibrium concentrations of thiosulfate solutions containing cadmium ions, and the calculation of the instability constants of the thiosulfate complexes of cadmium by such a method. The $Cd(NO_3)_2$ solution was added before addition of thiosulfate. It was established by preliminary experiments that in the presence of a large

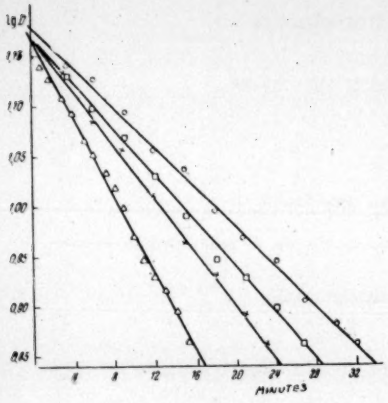

Fig. 1. Changes in optical density in the system $FeCl_3$ – $Na_2S_2O_3$ – KCNS.

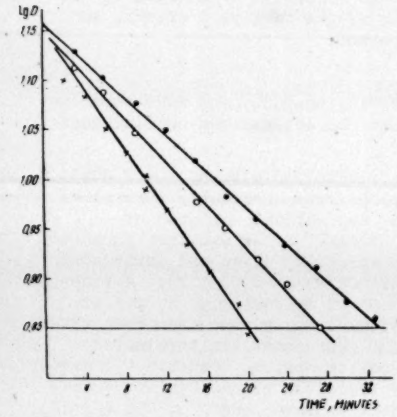

Fig. 2. Changes in optical density in the system $FeCl_3$ – $Na_2S_2O_3$ – $Cd(NO_3)_2$ – – KCNS.

excess of cadmium nitrate in solution, reaction (1) practically stops; for the $Cd(NO_3)_2$ range we studied, viz. $1.25 \cdot 10^{-3}$ M to $1.98 \cdot 10^{-3}$ M, there is a fall in the rate of the reaction studied. Determination of optical density was carried out in the same way as in the previous instance. All the values for one experiment lie on one curve on the graphs of time – logarithm of optical density (Fig. 2).

Two solutions were prepared in each test for studying the possibility of determining copper by the method of catalytic analysis; $FeCl_3$, KCNS, and $Na_2S_2O_3$ (as indicated above) were added to the first, while to the second was added the same amounts of these same materials plus a solution of $CuSO_4$ in such amount that the total concentration of this salt, after making the solution up to volume, varied within the limits of $4 \cdot 10^{-6}$ M to $2.4 \cdot 10^{-5}$ M.

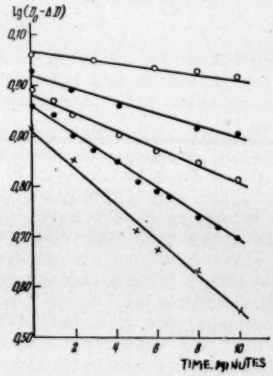

Fig. 3. Change in optical density in the system $FeCl_3$ – $Na_2S_2O_3$ – – $CuSO_4$ – KCNS.

Both solutions were poured into the photometer cell and the difference in optical density (ΔD) measured. The optical density of the solution was then determined in the absence of catalyst; the difference $D_0 - \Delta D$ was used for characterization of the velocity of the catalytic reaction, where D_0 is the optical density of the solution in the absence of catalyst at the end of the test. The concentrations of reactants were chosen so that the rate of the catalytic reaction could be measured in the course of 10-15 minutes, while the normal reaction proceeds as slowly as possible. (The concentrations after making up to volume were: $FeCl_3$ – $2.33 \cdot 10^{-4}$ M, KCNS – 0.0242 M, $Na_2S_2O_3$ – – $8 \cdot 10^{-4}$ M). Graphs of time – $\log(D_0 - \Delta D)$ were then constructed on the basis of the results obtained (Fig. 3).

DISCUSSION OF RESULTS

On the basis of the results obtained it is possible to establish that for the range of concentrations studied, the reaction between trivalent iron and thiosulfate follows the kinetic equation

$$-\frac{d[Fe^{3+}]}{dt} = k[S_2O_3^{2-}]^2 [Fe^{3+}]. \qquad (1)$$

It can be postulated that formation of the complex $[Fe(S_2O_3)_2]^-$ precedes oxidation of thiosulfate to tetrathionate, the ions of thiosulfate being orientated in this complex ion in such a way that the ion $S_4O_6^{2-}$ is easily formed subsequently. Apparently, synthesis of the unstable particle $M(S_2O_3)_2^{2-}$, which is capable of further reduction, precedes formation of tetrathionate from thiosulfate in all cases. E.g., formation of intermediate products during the oxidation of thiosulfate by iodine has been established [5]. The catalytic action of divalent copper salts can also be explained by the formation of an intermediate complex $Cu(S_2O_3)_2^{2-}$, which reacts further with Fe^{3+} ions. Formation of stable complexes with thiosulfate not only does not speed up the reaction, but even slows it down as a result of a decrease in concentration of $S_2O_3^{2-}$ ions. Such a phenomenon is observed, e.g., on addition of cadmium salts to test solutions.

On integrating equation (1) we get:

$$\log a - \log x = k c^2_{S_2O_3} t, \qquad (2)$$

where a is the initial concentration of iron salts, x – the concentration of iron salts at a given moment, k – a constant. In the given instance $k = 1.44 \cdot 10^4$ liter/mole^2/ minute.

Methods of calculating the concentration of test element in such cases have already been considered [6]. In the given case, thiosulfate concentration can be found from the equation:

$$c_{S_2O_3} = 0.0083 \sqrt{y}, \qquad (3)$$

where y is the absolute value of the slope of the straight lines $x - \log D$ (D – the optical density).

Table 1 contains results of the calculation of thiosulfate concentrations by means of this equation. The difference between calculated and experimental results nowhere exceed $\pm 3.5\%$. The method is applicable to concentrations of thiosulfate of the order 10^{-3} M.

TABLE 1

Determination of thiosulfate concentrations from results of kinetic determinations

Test number	Thiosulfate concentration, in mM/liter ($10^3 c_{S_2O_3}$)	y (slope of the straight line t − log D)	Thiosulfate concentration, in mM/liter ($10^3 c_{S_2O_3}$)	Deviation, in %
1	0.80	$0.99 \cdot 10^{-2}$	0.83	+3.7
2	0.88	$1.15 \cdot 10^{-2}$	0.89	+1.1
3	0.96	$1.34 \cdot 10^{-2}$	0.96	0.0
4	1.04	$1.56 \cdot 10^{-2}$	1.04	0.0
5	1.12	$1.70 \cdot 10^{-2}$	1.09	-2.7
6	1.20	$1.98 \cdot 10^{-2}$	1.17	-2.5

TABLE 2

Study of the equilibrium $CdS_2O_3 \rightleftharpoons Cd^{2+} + S_2O_3^{2-}$ kinetically (initial concentration of thiosulfate in all experiments $1.60 \cdot 10^{-3}$ M)

Initial concentration of cadmium nitrate, in mM/liter	y (slope of the straight line t − logD)	Equilibrium concentrations, in mM/liter			Instability constant of CdS_2O_3
		$S_2O_3^{2-}$	Cd^{2+}	CdS_2O_3	
1.98	0.90	0.79	1.17	0.81	$1.14 \cdot 10^{-3}$
1.73	1.09	0.87	1.00	0.73	$1.19 \cdot 10^{-3}$
1.80	1.14	0.89	1.09	0.71	$1.36 \cdot 10^{-3}$
1.59	1.24	0.93	0.92	0.67	$1.27 \cdot 10^{-3}$
1.51	1.38	0.98	0.89	0.62	$1.40 \cdot 10^{-3}$
1.25	1.50	1.02	0.68	0.58	$1.20 \cdot 10^{-3}$

Mean $(1.26 \pm 0.13) \cdot 10^{-3}$

TABLE 3

Determination of copper concentration kinetically

$CuSO_4$ concentration, in M/liter	y (slope of the straight line t − log D) ($D_0 - \Delta D$)	Calculated concentration of $CuSO_4$, in M/liter	Deviation, in %
$4.0 \cdot 10^{-6}$	$0.55 \cdot 10^{-2}$	$3.85 \cdot 10^{-6}$	-3.8
$8.0 \cdot 10^{-6}$	$1.18 \cdot 10^{-2}$	$8.2 \cdot 10^{-6}$	+3.1
$12.0 \cdot 10^{-6}$	$1.77 \cdot 10^{-2}$	$12.4 \cdot 10^{-6}$	+3.3
$20.0 \cdot 10^{-6}$	$2.70 \cdot 10^{-2}$	$18.9 \cdot 10^{-6}$	-5.5
$24.0 \cdot 10^{-6}$	$3.53 \cdot 10^{-2}$	$24.7 \cdot 10^{-6}$	+2.9

The method described for determination of concentration is suitable for studying equilibrium in systems in which thiosulfate participates. As an example we adduce results obtained during a study of the equilibrium of the dissociation of CdS_2O_3:

$$CdS_2O_3 \rightleftharpoons Cd^{2+} + S_2O_3^{2-}. \qquad (II)$$

In the systems studied the total concentration of the cadmium (c^o_{Cd}) and the total concentration of thiosulfate ($c^o_{S_2O_3}$) are known. The straight lines $\log D - t$ were drawn by the method described above, their slopes determined, and the equilibrium concentrations of thiosulfate ($\bar{c}_{S_2O_3}$) determined by means of equation (3). The concentration of the complex compound is obviously equal to the difference $c^o_{S_2O_3} - \bar{c}_{S_2O_3}$, while the concentration of free cadmium ions is given by

$$c^o_{Cd} - c^o_{S_2O_3} + \bar{c}_{S_2O_3}.$$

The instability constant of CdS_2O_3 was calculated by means of the equation:

$$\frac{(c^o_{Cd} - c^o_{S_2O_3} + \bar{c}_{S_2O_3})\,\bar{c}_{S_2O_3}}{(c^o_{S_2O_3} - \bar{c}_{S_2O_3})} = K. \qquad (4)$$

Values of the instability constant determined in this way are given in Table 2.

The values given for the instability constant relate to solutions with an ionic strength of the order of 0.11.

When the activity coefficients of Cd^{2+} and $S_2O_3^{2-}$ were calculated by means of Gugenheim's formula as modified by Davies [7], the instability constant related to a zero ionic strength was shown to be $(1.4 \pm 0.2)\cdot 10^{-4}$. This value is practically the same as that determined previously [8].

The reproducibility of the results is so good that such a method could be used for the determination of cadmium in solution.

On addition of copper salts to the solution, the reaction rate increases rapidly. The rate of the catalytic reaction obeys the equation:

$$-\frac{d[Fe^{3+}]}{dt} = \kappa\, c_{Cu} c^2_{S_2O_3} c_{Fe}, \qquad (5)$$

where κ is the catalytic coefficient. According to our measurements $\kappa = (2.1 \pm 0.2)\cdot 10^9$ (time in minutes, concentration in mole/liter).

The slopes of the straight lines $\underline{t}$ (time) $-$ $\log(D_o - \Delta D)$ were substituted in the equation:

$$c_{Cu} = a\underline{y}, \qquad (6)$$

where $\underline{a} = \frac{1}{\kappa c^2_{S_2O_3}}$ (in the given instance $\underline{a} = 7.0\cdot 10^{-4}$), while $\underline{y}$ is the slope of the straight line $\log (D_o - \Delta D)$ – time.

Values for copper concentrations as determined from equation (6) are given in Table 3. The deviation nowhere exceeds 5.5%.

In our previous article [6] we pointed out that the minimum concentration which can be determined by this method can be found from the equation

$$c_{min} > 0.1\,\frac{\underline{k}}{\kappa}.$$

Substituting the values of $\underline{k}$ and κ given above in this equation we get

$$c_{Cu\ min} > 7\cdot 10^{-7}\ M,$$

which corresponds to 0.4 μg in 10 ml.

SUMMARY

1. Oxidation of thiosulfate by trivalent iron has been studied, and a kinetic equation has been derived on the basis of which a method has been suggested for the determination of equilibrium concentrations of thiosulfate in solution.

2. Equilibrium concentrations of thiosulfate in solutions containing cadmium have been determined by a kinetic method. The instability constant of CdS_2O_3 was calculated and shown to be equal to $(1.4 \pm 0.2) \cdot 10^{-4}$.

3. A kinetic equation has been derived for the catalytic oxidation of thiosulfate by trivalent iron in the presence of copper, and the limiting concentration of copper which can be determined by catalytic analysis calculated.

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THE USE OF β-HYDROXYNAPHTHYL ALDEHYDE IN ANALYTICAL CHEMISTRY

1. GRAVIMETRIC AND VOLUMETRIC SEMI-MICRO DETERMINATION OF MAGNESIUM

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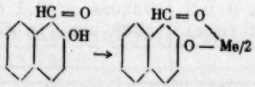
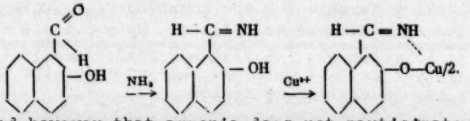
Salicylaldehyde has been used since 1930 as a reagent for Cu^{2+} [1], Fe^{3+} [2], and others [3-5]. Terentev and Rukhadze [6], have made a study of the analytical properties of derivatives of this aldehyde.

Experiments which we carried out on hydroxy aldehydes with condensed rings showed that β-hydroxy-α-naphthyl aldehyde in alkaline media forms inner complex salts with many divalent cations: Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}. [1] A six-membered ring is formed during the formation of these inner complex compounds



(1)

At the beginning of our tests we postulated that β-hydroxynaphthyl aldehyde (I) forms an immine compound with ammonia, similar to that formed by salicylaldehyde, which then reacts with an ion of a divalent cation, e.g.



Experiments showed however that ammonia does not participate directly in the formation of an inner complex compound, but only changes the pH of the medium.

β-Hydroxynaphthyl aldehyde precipitates Cu^{2+} and Ni^{2+} not only in the presence of ammonia, but even in the presence of pyridine and piperidine; Mg^{2+} can be precipitated with borax also.

In the present article we described semi-micro gravimetric and titrimetric methods of determining magnesium.

Synthesis of β-Hydroxy-α-naphthyl Aldehyde

30 g NaOH is dissolved in a mixture of 60 ml water and 45 ml alcohol, 14.4 g (0.1 M) of β-naphthol is then added, followed dropwise by 10 ml chloroform; the mixture is heated, commencement of the reaction can be confirmed by the appearance of a blue-green color. The heat generated during this reaction

1) Work along these lines is being continued.

is sufficient to keep it going. The temperature should not exceed 65°. The reaction is completed by heating the mixture for a short time on a water bath. Completion of the reaction is signalled by a change from blue to light red. The alcohol is distilled off and the pasty mass obtained acidified with hydrochloric acid (1:3). The hydroxyaldehyde which separates out as an oil is extracted with ether, the ether solution is dried over sodium sulfate and ether then removed by distillation. The aldehyde is distilled over the range 139-142° under a vacuum (4ml): Melting point 79-80° [for details see "Synthesis of Organic Compounds" Vol. 3, Foreign Literature Press (1952), 365 .

TABLE 1

Analysis of the Compound Prepared

Weight of sample, in g	Products formed, in g	Percentage found	
0.1408	0.3623 CO_2	C	70.22
0.1206	0.3101 CO_2	C	70.15
0.1408	0.0503 H_2O	H	4.00
0.1206	0.0420 H_2O	H	3.90
0.0520	0.1538 $Mg_2P_2O_7$	Mg	6.70
0.4870	0.1458 $Mg_2P_2O_7$	Mg	6.54

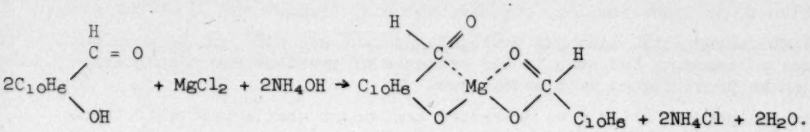
Preparation of the Magnesium Complex of β-Hydroxynaphthyl-Aldehyde

To 50 ml of a 0.1 M $MgCl_2$ solution was added 100 ml of a 1 M alcoholic solution of β-hydroxynaphthyl aldehyde followed by 5 ml of 10% ammonium chloride solution. The solution was heated to 60° and 5 ml of 25% ammonia added. Almost immediately a characteristic fine green-yellow crystalline precipitate appeared (Table 1).

TABLE 2

Weight of the magnesium complex of β-hydroxynaphthyl aldehyde, in g	Volume of 0.1 N HCl added, in ml	Volume of 0.1 N NaOH used, in ml	Volume of 0.1 N HCl used for the reaction, in ml
0.2936	20	4	16

Assuming the following formula for the compound: $C_{22}H_{14}O_4Mg$, the percentages of the respective elements are as follows: Mg – 6.63; C – 70.06; H – 3.85. Analysis of the compound for nitrogen gave negative results. On the basis of the analytical results obtained, the equation for the chemical reaction which occurs can be written as follows:



To confirm this formula, the compound obtained was dissolved in 0.1 N HCl and excess acid titrated with 0.1 N NaOH, using methyl red as an indicator (0.2% solution in 90% alcohol).

The results obtained are given in Table 2.

TABLE 3

Properties of the Magnesium Complex of β-Hydroxynaphthyl Aldehyde

Color	Light yellow
Solubility in water at 15°	0.006%
Solubility in alcohol at 15°	0.01
Solubility in ether at 15°	Insoluble
Heating in a capillary in air	Does not change up to 220°, chars on heating further
Behavior with dilute acids	Dissolves in acid, reforms on neutralization
Behavior with dilute alkali	On heating with 1 N NaOH a precipitate of $Mg(OH)_2$ forms

Consequently, 2 g equivalents of acid were used for decomposing 1 mole of the magnesium complex of β-hydroxynaphthyl aldehyde [1]. If there were two immine nitrogens in the molecule of this complex salt, then the amount of acid used up would be twice as much, and in the given instance 32 ml and not 16 ml of 0.1 N HCl would have been used. Thus, 1 ml of 0.1 N HCl corresponds to 0.001216 g of Mg or 0.01833 g of $C_{22}H_{14}O_4Mg$. Some of the properties of the compound prepared are given in Table 3.

The appearance of the crystals under the microscope is shown in the accompanying photograph.

Gravimetric Determination of Magnesium as the Magnesium Complex of β-Hydroxynaphthyl Aldehyde (I) in Pure Salts

A standard solution of magnesium containing 1 mg magnesium per ml was prepared by dissolving pure magnesium metal in hydrochloric acid.

To a definite volume of magnesium chloride solution was added 0.2 g of ammonium chloride on a knife tip; alcohol was then added in such amount that the solution was 50% with respect to it, finally, about 0.5 ml of concentrated ammonia was added. The solution was heated to 60° when a 2% alcoholic solution of β-hydroxynaphthyl aldehyde was added gradually, 2 ml of reagent solution being added per milligram of magnesium in the test solution. A crystalline precipitate with a yellow-green color formed either immediately or after some time. It was sometimes necessary to scrape the sides of the container with a glass rod to accelerate precipitation. After 30-35 minutes the precipitate was filtered through a No. 2 or No. 3 glass crucible, the residue was washed with 50% alcohol solution. The precipitate was washed twice with the same solution and dried at 125-130° to constant weight. When the precipitate is allowed to stand the solution can sometimes acquire a dark color; this however does not affect the results. The factor for conversion to magnesium is 0.06633. The results given in Table 4 show that for gravimetric determinations of magnesium in pure salts with β-hydroxynaphthyl aldehyde, experimental error does not exceed limits tolerated in analysis.

Determination of Magnesium in Minerals

This gravimetric method of determining magnesium was checked on natural minerals containing magnesium (carnallite). 5.6042 g of carnallite was dissolved

Crystals of the magnesium complex of β-hydroxynaphthyl aldehyde (magnification X 120)

TABLE 4

Determination of Magnesium as the Magnesium Complex of β-Hydroxy naphthyl Aldehyde (I) in Pure Salts

Amount of Mg, in mg	Weight of precipitate formed, in g	Mg found, in mg	Absolute error, in %
2	0.032	2.13	+0.13
3	0.0462	3.06	+0.06
3	0.0432	2.87	-0.13
4	0.0604	4.006	+0.006
5	0.0734	4.87	-0.13
5	0.0736	4.88	-0.12
5	0.0734	4.87	-0.13
6	0.0884	5.86	-0.14
6	0.0902	5.98	-0.02

in 250 ml water. The magnesium content was determined beforehand by the 8-hydroxyquinoline and pyrophosphate methods and found to be 7.25%. The method used for determining the magnesium was the same as that used for the pure salts.

The results obtained are given in Table 5.

Analysis of these results indicate a close agreement between the proposed method and the classical pyrophosphate method.

TABLE 5

Determination of Magnesium in Carnallite as the Magnesium Complex of β-Hydroxynaphthyl Aldehyde (I)

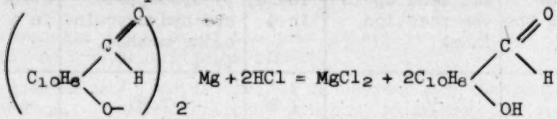
Volume of test solution (5 ml)

Weight of precipitate formed, in g	Mg found, in %	Mg found by the 8-hydroxyquinoline and pyrophosphate methods, in %	Deviation, in %
0.1220	7.20	7.25	-0.05
0.1224	7.24	7.25	-0.01
0.1218	7.0	7.25	-0.05

Volumetric Determination of Magnesium

This method is based on the interaction of the magnesium complex of β-hydroxy naphthyl aldehyde (I) with acids. If an exact amount of acid is used, the excess acid can be determined by titration with alkali, using methyl red as indicator.

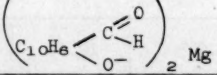
The reaction proceeds as follows :



Thus 1 ml of 0.1 N acid corresponds to 0.001215 g of magnesium or 0.01833 g of the complex salt. This method for magnesium was checked on pure salts. Precipitation of magnesium with β-hydroxynaphthyl aldehyde was effected as in the gravimetric method, the only difference being in that the precipitate was filtered off and washed with 50% alcohol on the No. 3 glass crucible. Crucible plus damp precipitate were then transferred to a 250 ml conical flask to which was added 40 ml of alcohol and 20 ml of 0.1 N hydrochloric acid. On careful shaking of liquid and crucible in the flask, the precipitate of the magnesium complex of β-hydroxynaphthyl aldehyde dissolved fairly quickly, and the solution became completely transparent. 6-7 drops of methyl red were added to this solution. Excess hydrochloric acid was then titrated with 0.1 N sodium hydroxide to the point where an orange color appeared. Results for the determination of magnesium in the pure chloride are given in Table 6.

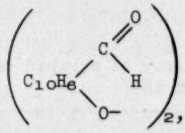
TABLE 6

Determination of Magnesium by an Acidimetric Method after Precipitation of Magnesium as

after Precipitation of Magnesium as 

Amount of Mg, in mg	Volume of 0.1 N NaOH used for neutralizing the HCl, in ml	HCl used up in the reaction, in ml	Mg found, in mg	Error, in (%)
3	17.28	2.72	3.3	+0.3
4	16.67	3.33	4.05	+0.05
5	15.89	4.11	4.99	−0.01
5	16.06	3.94	4.79	−0.21
6	15.07	4.93	5.99	−0.01
6	15.05	4.95	6.01	+0.01
7	14.16	5.84	7.09	+0.09

The results given in Table 6 show that after precipitation of magnesium as



its quantitative determination can be finished off volumetrically. The applicability of this method to the determination of magnesium was checked on a solution of carnallite.

TABLE 7

Determination of Magnesium with β-Hydroxynaphthyl Aldehyde in Carnallite.

5.604 g of carnallite was dissolved in 250 ml of water

Volume of test solution of carnallite in ml	Volume of 0.1 N NaOH used for neutralizing the HCl, in ml	Volume of 0.1 N HCl used up in the reaction, in ml	Mg found, in %	Mg found by the pyrophosphate and hydroxyquinoline method, in %	Absolute error, in %
4	14.64	5.36	7.26	7.25	+ 0.01
5	13.31	6.69	7.25	7.25	0

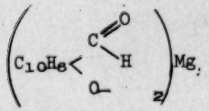
TABLE 8

Determination of Magnesium in Sedimentary Rocks, Volumetrically

Weight of sample in 100 ml of solution, in g	Volume of 0.1 N NaOH used for neutralizing the HCl, in ml	Volume of 0.1 N HCl used up in the reaction, in ml	Mg found, in %	Mg found by the pyrophosphate and hydroxyquinoline methods, in %	Absolute error, in %
1	15.025	4.975	12.09	11.97	+0.12
0.8	16.41	3.59	10.90	10.89	+0.01
0.8	16.46	3.54	10.75	10.89	−0.04
2.87	16.1	3.90	3.30	3.46	−0.16
2.87	16.25	3.75	3.17	3.46	−0.29
2.50	15.15	4.85	4.71	4.55	+0.16

Results of these determinations are given in Table 7.

The results given in Table 7 demonstrate the possibility of a rapid determination of magnesium by a combined method — separation as



with subsequent solution of the precipitate in 0.1 N HCl (a measured amount), and titration of excess acid with alkali.

Magnesium was also determined in sedimentary carbonate rocks which, in addition to magnesium, contained silicon, calcium, aluminum, and iron.

0.5 - 2.5 g of material, according to its magnesium content, was dissolved in hydrochloric acid, and insoluble material filtered off. After removal of aluminum and iron by the normal method as hydroxides, the precipitate was carefully washed with hot water and the filtrate containing calcium and magnesium made up to 100 ml with water. To precipitate calcium as the oxalate, 5 ml of the filtrate was heated to 80° and a small excess of a 4% solution of ammonium oxalate gradually added to it. After a short time the precipitate was filtered, washed with water, and the filtrate containing magnesium evaporated to 10-13 ml; alcohol was not added in this instance, but the other operations used for precipitation and determination of magnesium were the same as those described above. Results are given in Table 8.

These results show that magnesium can be determined in sedimentary rocks.

Magnesium was determined in alloys such as electron metal. The alloy was dissolved in hydrochloric acid, and after removal of aluminum with ammonia, magnesium was determined in the filtrate by the method described above. The percentages of magnesium found were 90.30% and 90.37%; while the percentage found by the hydroxyquinoline and pyrophosphate methods was 90.9%.

SUMMARY

1. A quantitative method of determining magnesium has been developed in which magnesium is precipitated with β-hydroxynaphthylaldehyde in an ammoniacal-alcoholic medium; the precipitate is ether weighed or a volumetric finish is employed.

2. Magnesium can be determined with β-hydroxynaphthyl aldehyde in alloys and rocks.

3. Quantitative determination of magnesium with β-hydroxynaphthylaldehyde is characterized by its speed, particularly when a volumetric finish is used.

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DETERMINATION OF FLUORINE IN ORGANIC COMPOUNDS

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The need for a rapid and accurate method of determining fluorine in organic compounds has led to the appearance of a large number of papers devoted to this question, whichhave been reviewed in detail by Nikolaev [1].

Of recent papers, mention must be made of that of Clark [2], in which the fluorine is determined by combustion of test material in a quartz tube using a platinum catalyst at 900° in an oxygen atmosphere, followed by titration of the acid combustion products with alkali. According to this author, the presence of nitrogen, phosphorus, or sulfur leads to erroneous results.

Gelman and Korshun [3] have developed a method for the simultaneous determination of fluorine, carbon, and hydrogen based on combustion of test material in a stream of oxygen or air, and absorption of fluorine by magnesium oxide as the high melting fluoride. Despite its simplicity this method is inapplicable to materials containing sulfur and other halogens as well as fluorine, or to mixtures of fluorine derivatives with other materials containing these same elements.

In practice this last case is of special interest, since many fluorine-containing compounds which are of great technical importance may contain varying amounts of chlorine-containing contaminants.

In the present article a method is described for the determination of fluorine in organic compounds, based on decomposition of the organic material and subsequent titration of the fluoride formed with a solution of zirconium chloride under conditions described by Zeppelin [4]. This method permits determination of fluorine in the presence of chlorine, nitrogen, and sulfur.

A complication which arose on applying this method to organic compounds was the difficulty of decomposing the fluorine-containing compounds with a view to converting the fluorine quantitatively to a fluoride.

Of the various methods used for mineralization of organic compounds which contain fluorine, the one most often used is decomposition of test material at a high temperature in a nickel or platinum bomb by means of various oxidizing agents or alkaline compounds: sodium peroxide, sugar and potassium nitrate [5], metallic sodium [6], and metallic potassium [7].

Attempts to use method [6] for mineralization of the fluorine-containing compounds we were interested in were unsuccessful. On heating the fluorine-containing material at the temperature indicated by the author (600-700°), the analytical results varied considerably and were much lower than the theoretical values. On heating the bombs in a strong gas burner flame, the latter was colored an intense yellow (indicating loss of sodium through the bomb case), and even lower results were obtained.

Korshun and Gelman [8], pointed out the special advantages of decomposing organic materials with metallic potassium for purposes of micro- and semi-micro analysis. As a consequence of this we studied the decomposition of fluorine-containing

compounds with metallic potassium in nickel bombs. The decomposition method was very similar to the method of Korshun and Chumachenko described in [8]. Nevertheless, in contrast to these authors, who recommended decomposition of halogen containing material by heating the bomb to a red heat for 15-20 minutes, it was shown experimentally, using 1-trifluoromethyl-3-acetaminobenzene as an example, that in order to decompose the sample completely with quantitative conversion of organically combined fluorine to potassium fluoride, it is essential to heat the bomb for 2 hours at 900-950°. At lower temperatures (ca. 800-830°) the results obtained were low. This was confirmed further on a number of other compounds.

EXPERIMENTAL

Description of the Method

A nickel bomb [8] was used for the determination of fluorine in organic compounds. Before starting a test, the bomb was cleaned and heated to a red heat. To ensure hermetical sealing, copper washers were used, these being changed after each determination. The bomb flanges were carefully cleaned with emery paper. When liquids were analyzed, they were weighed out from a Lunge micro pipet. When an aliquot of test material had been loaded into the bomb, 2-3 times its amount of potassium metal was introduced. The potassium must be added in the form of small lumps washed beforehand with dry ether. The bomb was then closed and heated for 2 hours in an electric oven at 900-950°. After heating, the bomb was removed, cooled in air, and opened. The bomb case was placed in a test tube 20 cm long and 4.5 cm in diameter, water was then carefully introduced into the bomb dropwise until the vigorous reaction with residual potassium had ceased. When reaction was complete the contents of the bomb were carefully stirred with a glass rod. The contents were then filtered free from carbonized particles through a No. 2 or No. 3 glass filter into a 250 ml Bunsen flask. The copper washer, bomb case, and test tube were all carefully washed and the washings also passed through the filter. The contents of the Bunsen flask were quantitatively transferred to a 200 ml conical flask and made up to a volume of 140-150 ml with water. 2 drops of a 0.5% solution of sodium alizarinsulfonate were added and the solution neutralized by dropwise addition of 10% chemically pure hydrochloric acid from a buret till the solution acquired a pale rose color. If one drop too much of hydrochloric acid is added the solution becomes a bright yellow. After neutralization the solution was heated for 1-1.5 hours on a boiling water bath, cooled, and the volume made up to 150 ml. 4 drops of a 0.5% solution of sodium alizarinsulfonate were then added again. The color changed to an intense red-violet. 1-2 drops of 10% hydrochloric acid were added until a light yellow color was obtained, the solution was then titrated with a solution of zirconium chloride from a micro buret until the solution changed from a bright yellow to a brownish yellow. When this color was observed the zirconium chloride solution was added 1 drop at a time at intervals of 5 minutes to the appearance of a permanent rose color. When the rose color remained for 5 minutes and did not fade, but on the other hand intensified, the titration was considered complete.

Zirconium chloride solution was prepared and standardized with chemically pure sodium fluoride as recommended in [4].

When compounds containing sulfur were analyzed the solution, after neutralization with hydrochloric acid to a weak rose color, was heated on a boiling water bath for complete removal of hydrogen sulfide (1-1.5 hours), cooled, and filtered free from the precipitate of metal sulfides formed from the material of the apparatus and washers, by passing it through a No. 3 sintered glass filter; it was then made up to 150 ml and the procedure described above followed.

Results obtained by this method are given in the table.

TABLE

Compound	Formula of compound	F calculated, in %	F found, in %	Difference, in %
1-Trifluoromethyl-3-acetaminobenzene	$C_9H_8ONF_3$	28.05	27.98 27.88 27.73	−0.07 −0.17 −0.32
5-Trifluoromethyl-3-aminobenzoic acid	$C_8H_6O_2NF_3$	27.78	27.93 27.80	+0.15 +0.02
Methyl 5-trifluoromethyl-3-aminobenzoate	$C_9H_8O_2NF_3$	26.01	25.87 25.97 25.76	−0.14 −0.04 −0.25
2-Nitro-4-trifluoromethylphenylethylsulfone	$C_9H_8O_4NSF_3$	20.12	20.23 20.14 20.16	+0.11 +0.02 +0.04
1-(3'-Carboxyphenyl)-3-trifluoromethylethylpyrazolone-5	$C_{11}H_7O_3N_2F_3$	20.94	20.62 21.08 20.96	−0.32 +0.14 +0.02
1-(4'-Carboxyphenyl)-3-trifluoromethylpyrazolone-5	$C_{11}H_7O_3N_2F_3$	20.94	20.84 20.62	−0.10 −0.32
1-(3'-Trifluoromethylphenyl)-3-methylpyrazolone-5	$C_{11}H_9ON_2F_3$	23.53	23.41 23.31 23.61	−0.12 −0.22 +0.08
1-(3'-Trifluoromethylphenyl)-3-trifluoromethylpyrazolone 5	$C_{11}H_6ON_2F_6$	38.49	38.33 38.47 38.41	−0.16 −0.02 −0.08

SUMMARY

A method is described for the determination of fluorine in organic compounds containing chlorine, nitrogen, and sulfur.

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DETERMINATION OF FLUORINE IN ORGANIC COMPOUNDS

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In order to analyze fluoro-organic compounds it is necessary not only to solve the problem of determining the fluoride ion, but also to find how to decompose these compounds. Compounds which contain more than one atom of fluorine per carbone atom are particularly difficult to decompose. Such compounds often possess high thermal stability and consequently extremely drastic decomposition methods are necessary to break down the C=F bond. Moreover when fluorocarbons are thermally decomposed, formation of the very stable compound CF_4 is possible.

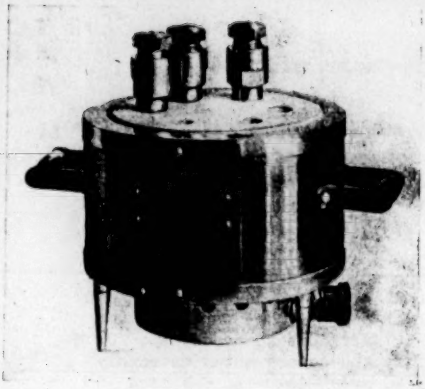
According to published results [1], CF_4 and fluorocarbons with higher molecular weights react with alkali metals at temperatures ca. 400° to form fluorides and carbon. Various methods of determining halogens including fluorine [2-6], have been developed on this basis.

In 1946 we worked out a semi-micro quantitative method for fluorine based on the interaction of fluoro-organic compounds with potassium metal in a closed space, but at higher temperatures (800-850°). Subsequent determination of fluoride ion was carried out volumetrically. Quantitative decomposition was achieved in a few minutes independently of elemental composition and molecular structure. The metal reacts with the products of thermal decomposition in the vapor phase; this ensures a fairly rapid reaction rate and makes it an effective method for the elemental analysis of organic compounds.

Decomposition. Aliquot samples of 8-25 mg, according to the percentage content of fluorine in the test sample, were heated with 4-5 times their amount of metallic potassium in a steel micro-bomb at 800-850° for 10-15 minutes. Heating was carried out in a special electric oven into which six bombs could be loaded simultaneously (see diagram). The construction of the bomb and subsequent treatment of the melt have already been described previously when describing the method of determining halogens [3], and simultaneous determination of other elements [6]. For constructing the bomb, stainless steel of the following grades were used: EYaI-T for the tube, EZh-4 for the hemispherical surface, and 40-X for the stopper and connecting nozzles. If the bomb is carefully hermetically sealed during daily use, it may serve for a year or more.

Determination of the Fluoride Ion

The most widely used method for determination of fluorine is the gravimetric one in which fluoride is precipitated as lead chlorofluoride [2, 5, 7, 8]; this method can be regarded as the best because of the high value of the conversion factor to fluorine. Nevertheless, major drawbacks of this method are the time taken to filter the precipitate, and, in addition, the complications which arise when other ions are present, which are either adsorbed on the precipitate surface or interact with lead, thereby lowering



the accuracy of the method. Of the volumetric methods the one that we were most attracted to was titration of fluoride with thorium nitrate [9-14].

Titration conditions must be strictly identical with those used for titration of the blank, which at the same time serves as an indicator during titration of fluoride. To each 10-25 ml aliquot of test solution 0.4 ml of a 0.1% aqueous solution of sodium alizarinsulfonate was added; the solution was neutralized to a lemon-yellow color by dropwise addition of 1:50 nitric acid; 2.5 ml of a buffer mixture was then added, the volume made up to 50 ml, and the solution finally titrated with a 0.025 N solution of $Th(NO_3)_4$ until the appearance of a pale rose color. The thorium nitrate was standardized by measuring the dry residue of ThO_2. A 10 ml micro buret with 0.02 ml scale divisions was used for titration. By reading the volume with a lens, it was possible to measure out with an accuracy of 0.005 ml.

The hydrogen ion concentration of the solution being titrated is of essential importance for the correct determination of the end point. A study of this question showed that the most accurate results are obtained at a pH of 2.9-3. Results of these experiments are given below.

Effect of pH on fluoride titration with 0.025 N $Th(NO_3)_4$.

50 ml of solution containing 1.203 mg of fluorine was titrated

pH	2.4	2.6	2.8	2.9	3.0	3.2	3.4	3.6
Fluorine determined in mg	1.311	1.286	1.240	1.212	1.206	1.143	1.107	1.025

A buffer solution prepared as follows was used to establish the requisite pH: 50 ml of a 1 N solution of monochloroacetic acid was neutralized with 1 N sodium hydroxide to a phenolphthalein end point; 50 ml more acid was then added and the volume made up to 250 ml. If, on measuring the pH of the buffered solution, the pH should be too high or too low the necessary amount of alkali or acid should be added to adjust the pH to exactly 2.9-3.

It is known that when thorium nitrate is titrated in the presence of sodium alizarinsulfonate, the color of the indicator changes somewhat later than the equivalence point, so that it is necessary to subtract the volume of solution used for the formation of the lake from the total volume of $Th(NO_3)_4$ used. Moreover, the color change of the indicator is related to the fluoride ion concentration in the solution being titrated. Consequently, in order to avoid too high results, it is necessary to determine a correction factor. We established these factors experimentally by titrating solutions of pure sodium fluoride with varying fluoride concentrations; the results of these experiments are given in Table 1.

TABLE 1

Volume of Solution Titrated 50 ml

Amount of 0.025 N $Th(NO_3)_4$ solution used (ml)	Correction to be applied to solution volume (ml)	Amount of 0.025 N $TH(NO_3)_4$ solution used (ml)	Correction to be applied to solution volume (ml)
0.200	0.075	3.000	0.130
0.500	0.130	3.500	0.100
1.000	0.200	4.000	0.100
1.500	0.190	5.000	0.100
2.000	0.180	8.000	0.100
2.500	0.160		

1 ml of 0.025 N $Th(NO_3)_4$ corresponds to 0.475 mg fluorine.

TABLE 2

Titration of Aliquot Portions After Decomposition of Teflon Weight of aliquot 23.919 mg; volume of solution after decomposition of the melt – 250 ml; volume of solution titrated 50 ml

Aliquot portions (ml)	Fluorine content (mg)	Fluorine content found (mg)
25	1.819	1.817
15	1.091	1.090
10	0.727	0.730
5	0.363	0.367
2	0.146	0.149
1	0.073	0.073

Despite the fact that the corrections are significant with respect to the total volume of $TH(NO_3)_4$ solution used, their application to the titration conditions which we have worked out permits fluoride to be determined with a sufficient degree of accuracy in the concentration range 0.1 to 3 mg in 50 ml of the solution being titrated (see Table 2).

Effect of Other Ions During Titration of Fluoride with $Th(NO_3)_4$

All ions which are capable of reacting with fluorine or thorium interfere with thorium nitrate titrations [15-17]. Sulfate and phosphate ions in particular interfere [17-19]. As regards chlorides and nitrates, interference on their part will be determined, to a large extent, by their concentration in the solution being titrated. Thus, according to Geyer [20], chlorides, nitrates and perchlorates do not interfere with titration when they are present in concentrations of 0.1–0.2 N. In the solutions which we obtained after washing out the melts, the ionic concentration was 0.01–0.005 N. Chlorides as well as bromides and iodides not only do not interfere with fluoride determination, but can be actually determined quantitatively alongside the fluoride by titrating separate aliquots [6]. When the test material contains sulfur, the latter is converted into sulfide during decomposition and does not interfere with fluoride determination. A large percentage of any nitrogen present in organic material is evolved as cyanide which does not interfere with fluoride titration either. Results of fluoride determinations in the presence of halogens, sulfur, and nitrogen, as well as of simultaneous determination of fluorine and chlorine, are adduced in Tables 3 and 4. Since we did not have at our disposal any compounds containing fluorine and sulfur in the same molecule, we analyzed mixtures of Teflon and naphthalenedisulfonic acid.

Effect of Phosphorus

Determination of fluorine in the presence of phosphorus has been studied by other authors [17,19], during the gravimetric determination of fluorine, by precipitating it as lead chlorofluoride. Determination of fluorine in the presence of phosphorus was also of interest under the conditions which we worked out. We carried out all our tests on mixtures of individual organic compounds containing fluorine and phosphorus.

In the course of our work it became clear that the transition point during titration of the fluoride ion in the presence of phosphorus was sharp enough, but it lagged behind the real equivalence point for fluoride, the extent of this lag being dependent on the amount of phosphorus present. It is highly probable that during decomposition of material containing phosphorus with potassium

TABLE 3

Determination of Fluorine in the Presence of Halogens, Sulfur, and Nitrogen

Test material	Weight taken (mg)	Volume of 0.025 N $Th(NO_3)_4$ used to titrate 0.1 g of material	Percent fluorine	
			Found	Difference
$C_4H_4N_3F_3$	14.218	1.389	46.43	0.09
Calculated: % F – 46.34	21.562	2.096	46.18	0.16
	25.775	2.513	46.33	0.01
$CF_3CFBrCOOCH_3$.....	18.178	1.207	31.64	0.16
Calculated: % F – 31.80	24.020	1.593	31.59	0.21
Mixture of $(C_2F_4)_x$ and $C_{10}H_6(SO_3H)_2$.....	22.095 + 23.273	3.520	75.87	0.12
Calculated: % F – 75.98	20.789 + 25.977	3.308	75.80	0.18

TABLE 4

Simultaneous Determination of Fluorine and Chlorine

Test material	Weight taken (mg)	Volume of 0.025 N $Th(NO_3)_4$ used for titrating 1/4 of the sample	% Fluorine		Volume of 0.01 N $Hg(NO_3)_2$ used for titrating 1/4 of the sample	Percent Chlorine	
			Found	Difference		Found	Difference
$C_4H_3Cl_3FNO$							
Calculated:	28.265	1.511	10.09	0.11	11.300	56.10	0.23
% F – 9.98	25.587	1.343	9.98	0	10.110	56.01	0.14
% Cl – 55.87							
$C_{10}H_8ClFN$							
Calculated	25.200	0.458	8.63	0.27	1.187	16.70	0.09
% F – 8.90	26.048	0.488	8.91	0.01	1.229	16.73	0.12
% Cl – 16.61	28.589	0.514	8.55	0.35	1.335	16.55	0.06

TABLE 5

Weight of sample (mg)	Volume of 0.025 N $Th(NO_3)_4$ used (ml) for 1/4 part of aliquot
24.710	0.365
23.268	0.315
21.233	0.400

metal, the phosphorus goes into a trivalent state. Nevertheless, the vigorous evolution of heat, and sometimes even explosions which we observed during dissolution of the melt in water, may lead to partial oxidation of phosphorus and partial loss as phosphine. All these factors prevented us previously from coming to any definite conclusion as to the presence of reproducible amounts of oxidizable phosphorus in each test material. Actually, when three samples of the same phosphorus compound were decomposed, varying amounts of thorium nitrate were used (Table 5).

As is evident from Table 5 the amount of thorium nitrate used to titrate the phosphorus should be established independently, i.e. for each solution of the melt obtained as a result of the decomposition of each separate aliquot of test material. Only by doing this is it possible to determine exactly the amount of thorium nitrate spent in titrating the fluoride. The solution of

TABLE 6

Determination of Fluorine in the Presence of Phosphorus

Mixture of materials	Weight taken (mg)	Volume of 0.025 N $Th(NO_3)_4$ used per 0.1 g of sample, in ml		Fluorine found in %	Difference in %
		I[1]	II		
Teflon and triphenylphosphine	15.121 + 14.142	2.627	0.210	75.85	0.13
Calculated: % F – 75.98	12.141 + 15.145	2.168	0.215	76.10	0.12
p-Trifluoromethyl-α-bromoacetophenone and triphenylphosphine	12.421 + 12.425	0.738	0.185	21.15	0.16
	17.220 + 13.140	0.971	0.195	21.40	0.09
	18.142 + 13.045	0.989	0.190	20.95	0.36
Calculated: % F – 21.31	20.217 + 15.140	1.100	0.215	20.80	0.10
p-Trifluoromethyl-α-acetoamino-β-hydroxypropiophenone and triphenylphosphine Calculated: % F – 20.70	12.145 + 14.610	0.734	0.200	20.90	0.20
p-Fluorobenzophenone and triphenylphosphine	15.145 + 15.190	0.513	0.215	9.35	0.14
	12.415 + 13.150	0.441	0.195	9.40	0.09
Calculated: % F – 19.49					

1) I – total amount of $TH(NO_3)_4$ used during titration of test without evaporation

II – volume of $TH(NO_3)_4$ used for titrating the test after evaporation

this problem was made easier in our method by the possibility of taking aliquot amounts of the final solution for titration. The total amount of thorium nitrate used and the amount of it used up in titrating phosphorus compounds were determined on parallel aliquot portions. Two aliquots were titrated as usual, while fluorine was removed from two other aliquots as follows: the aliquots were transferred to a porcelain beaker in which they were evaporated to dryness on a water bath, the residue was moistened with a few drops of concentrated hydrochloric acid and evaporated to dryness again. This treatment was repeated 2 – 3 times, after which the residue was dissolved in water, transferred to a titration flask and titrated in exactly the same way as the first pair of aliquot portions. The difference between the titers obtained is equal to the thorium nitrate used for titrating the fluoride. When such a technique is used there is no need for any further corrections and the results obtained are more accurate than usual. The method was checked on mixtures of fluoro-organic compounds with triphenylphosphine. Table 6 contains the results, which show that fluoride can be determined in the presence of phosphorus.

SUMMARY

A micro method is described for the determination of fluorine in organic

compounds, in which test material is heated with potassium metal in a steel micro bomb at 800 – 850° followed by titration of the fluoride formed with thorium nitrate. The presence of nitrogen, sulfur, and other halogens does not interfere with the titration.

It has been demonstrated that fluorine and chlorine can be determined simultaneously; a technique is also described for the determination of fluoride in the presence of phosphorus.

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A MERCURIMETRIC METHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

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The simplest and most widely used method of determining halogens in organic compounds is that of Stepanov [1], which is based on dehalogenation of the test compound in ethyl alcohol with metallic sodium, followed by titration of the liberated halogen ion with a silver nitrate. This method has been studied in detail by various authors, most of whom reckon it to be a sound method. Ruzhentseva and Letina [2], however pointed out the significant differences obtained between theoretical and experimental values for the halogens. In order to overcome difficulties connected with the fact that the reaction sometimes does not go to completion, several modifications have been suggested. Bacon [3], in particular, drew up special tables for calculating the amounts of metallic sodium and alcohol required for the weight of test material used. Some workers have used metallic potassium and a mixture of ethyl alcohol and benzene [4], while others have used higher alcohols [5], instead of sodium and ethyl alcohol. Amyl alcohol has a considerably higher boiling point, so that analyses can be carried out at higher temperatures. Nevertheless, observation has shown that under these conditions, the liquid turns brown toward the end of the test because of resinification of amyl alcohol. We showed however that dehalogenation with sodium metal goes a good deal smoother, even at ordinary temperatures, if the higher alcohol contains some ethylene glycol. Dehalogenation proceeds briskly enough in a 15% solution of ethylene glycol in isobutyl alcohol without heating, and it is only toward the end of the reaction that it becomes necessary to raise the temperature of the reaction mixture.

Another drawback of the Stepanov method and its many modifications is determination of halogen by the Volhard method, which, especially in the case of microdeterminations, is not accurate enough. The use of adsorption indicators [6] does not have any special advantages in this instance. In particular, only chloride can be determined argentometrically in the presence of bromophenol blue as suggested by Sisido and Jagi [5], for the micro determination of halogen containing compounds.

Determination of halide mercurimetrically is both more convenient and accurate.

Mercurimetric methods have only become of practical significance since diphenylcarbazide and diphenylcarbazone [9, 10], which form intensely violet colored compounds with divalent mercury in the presence of mineral acids, have replaced the indicators used earlier in turbidimetric methods [7, 8], for determining the equivalence point.

Mercury halides do not give colors under these conditions. Hg^{2+}, Cd^{2+} and Zn^{2+} ions do not affect the color.

The sensitivity of the mercurimetric method has been further increased by titrating the halides in alcoholic media [11]. Under these conditions, as a result of a decrease in the extent of dissociation of the mercury halides, the color change at the end point is much sharper. In order to determine the accuracy of the mercurimetric titration of halides in an alcoholic medium, measurements of small amounts of chloride have been carried

TABLE 1

Mercurimetric Determination of Small Amounts of Chloride in an Alcoholic Medium

Cl^- taken in μg	Cl^- found in μg	Error in %
124.6	124.5	− 0.08
134.7	134.4	− 0.22
202.1	201.6	− 0.25
258.3	257.3	− 0.38
269.5	268.8	− 0.25
303.2	303.2	0
381.6	381.9	+ 0.08

out using 0.01 N $Hg(NO_3)_2$ in the presence of diphenylcarbazone. Results are given in Table 1.

It is clear from Table 1 that the experimental error varies within the limits 0 − 0.38%. The accuracy of the results obtained during determination of bromide and iodide was of the same order. Thus titration in an alcoholic medium permits determination of halide with an accuracy greater than that possible by iodometric methods.

The use of higher alcohols, in particular of isobutyl alcohol, with glycol for dehydrohalogenation, and substitution of silver nitrate titration by a mercurimetric titration simplify the Stepanov method, make it more convenient, and permit its use for micro analysis.

EXPERIMENTAL

Reagents required

1) 15% solution by volume of ethyleneglycol in isobutyl alcohol.
2) Sodium metal.
3) Nitric acid, sp. gr. 1.165.
4) 1% alcoholic solution of diphenylcarbazone.
5) 0.05 N standard $Hg(NO_3)_2$.

5.5 g of mercuric oxide is moistened with a small amount of water, and 8 − 10 ml of concentrated nitric acid added dropwise (until the oxide is completely dissolved), the solution is then diluted with water to 1 liter, and filtered.

The $Hg(NO_3)_2$ solution is standardized as follows, 2 drops of the 1% alcoholic solution of diphenylcarbazone are added to 1 ml of 0.05 N sodium or potassium chloride measured out in a small beaker, the solution is acidified with 0.2 ml of 1 N nitric acid, and after addition of 5 ml 96° ethyl alcohol, it is titrated with $Hg(NO_3)_2$ from a microburet, till the appearance of a pale rose color.

Analytical procedure

The amounts of the respective reagents used for dehydrohalogenation depend on the nature of the halogen to be determined, i. e., whether the organic compound contains chlorine, bromine, or iodine.

For chloride determination the sample (ca. 0.1 g) is dissolved in 15 ml of the ethyleneglycol − isobutyl alcohol mixture in a 100 ml standard flask, and 2.4 g sodium gradually added in 5 − 6 lots. When half the sodium has been added, another 15 ml of the ethyleneglycol − isobutyl alcohol mixture is added in two lots, the rest of the sodium being added in between the two lots of solvent. Toward the end of the reaction the contents of the flask are carefully heated until the metal has dissolved. When all the halogen has been split off, 20 ml of water is added to decompose the alcoholate, and 18 ml of nitric acid (sp. gr. 1.165) added to neutralize the bulk of the sodium, 1 ml of acid is equivalent to 0.1 g sodium. The flask is stoppered and carefully shaken; after cooling, the volume is made up to the mark with

ethyl alcohol.

If the test material has a low boiling point or is volatile, a reflux condenser is used during dehydrohalogenation.

Decomposition of bromo compounds is carried out in a 50 ml standard flask. An aliquot of test material (ca. 0.1 g) is dissolved in 10 ml of ethyleneglycol – isobutyl alcohol mixture, and 1.0 g sodium gradually added. Before addition of the last bit of sodium a further 5 ml of solvent mixture is added. Toward the end of the reaction the solution is carefully heated, 10 ml of water and 8 ml of nitric acid are added to the cooled mixture, after cooling again the solution is made up to the mark with ethyl alcohol.

Determination of iodide is carried out in the same way as the bromide in a 50 ml standard flask. The aliquot of test material (ca. 0.1 g) is carefully mixed with 8 ml of 15% ethyleneglycol – isobutyl alcohol solution, 0.7 g Na gradually added. Toward the end of the reaction another 2 ml solvent mixture is added, and the flask contents heated until all the sodium has dissolved. To the still warm alcoholate 10 ml of water is added, and the alkali partly neutralized with 5 ml of nitric acid. After cooling, the solution is made up to 50 ml with ethyl alcohol.

TABLE 2

Analysis of Organic Compounds Which Contain Halogens

Test material	Weight taken in g	Halogen content in %		Difference between theoretical and experimentally determined values in %
		Found	Calculated	
Chlorobenzene....	0.10510	31.64	31.53	+ 0.11
	0.08677	31.34		– 0.19
	0.09877	31.35		– 0.18
Monochloroacetic acid	0.09508	37.40	37.53	– 0.13
	0.08954	37.74		+ 0.21
Dibromobenzene...	0.10231	67.69	67.76	– 0.07
	0.10784	67.82		+ 0.06
	0.08646	67.78		+ 0.02
α-Bromocamphor...	0.09923	35.26	34.59	+ 0.67
	0.09954	35.24		+ 0.65
Iodobenzene.....	0.10931	62.37	62.22	+ 0.15
	0.12154	62.03		– 0.19
	0.10676	62.41		+ 0.19
Iodoform.....	0.08078	96.58	96.68	– 0.10
	0.09154	96.54		– 0.14
	0.09922	96.83		+ 0.15

The second stage of the analysis-mercurimetric determination of halide is the same in all cases. 5 ml of the solution prepared as described above is measured accurately into a small beaker, 5 ml of ethyl alcohol followed by 2 drops of the 1% alcoholic solution of diphenylcarbazone are added, and the solution neutralized carefully with nitric acid of the same concentration. It is essential that neutralization be carried out very carefully so as to avoid excess acid. The solution is titrated with 0.05 $Hg(NO_3)_2$ from a micro buret to a pale rose color.

For titration it is most convenient to use a pneumatic tapless micro buret [12], constructed on the Shilov principle, which permits working with great accuracy and convenience.

If the reagents are not free from halide, a blank test should also be carried out.

A number of compounds were analyzed using this method (Table 2).

α-Bromocamphor, results of whose analysis are included in Table 2, is a technical product and the determination of its bromine content was of interest to us from the point of view of the reproducibility of the results.

The procedure described above is not the only possible technique. Initially we dehalogenated test material in an ordinary 150 – 200 ml Erlenmeyer flask, and titrated, after careful neutralization with nitric acid, all the solution in situ in the flask with 0.1 N $Hg(NO_3)_2$ from an ordinary buret. This technique also gave good results for the analysis of bromo- and iodo-organic compounds. Nevertheless, when we came to study chloro-organic compounds, we found that the end point was not sharp enough, presumably because of the large volume of solution to be titrated. This fact together with the desirability of making replicate titrations convinced us that we should use the technique described above, and finish off the determination with a micro titration.

The accuracy of the proposed method for determining halogen in halogen organic compounds is good enough to convert it into a micro-method and for carrying out analysis with aliquots not greater than 10 – 20 mg.

The tests we carried out showed that halogen can be determined accurately enough in organic compounds which contain only carbon, hydrogen and oxygen in addition to the halogens. Nitrogen and sulfur interefere with halogen determination, a fact not sufficiently stressed by other workers. It will be necessary to carry out additional work to study the effect of nitrogen and sulfur on analytical procedure.

SUMMARY

A method has been developed for the determination of halogens in organic compounds which is based on dehydrohalogenation of test material with metallic sodium in a mixture of ethyleneglycol and isobutyl alcohol, followed by mercurimetric determination of the halide ion. The method is convenient because of its simplicity and practicability.

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A METHOD FOR THE DETERMINATION OF RADIOACTIVE CARBON IN ORGANIC COMPOUNDS

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The radioactive isotope of carbon C^{14} is widely used as an isotopic indicator in chemistry for the study of reaction mechanism and other problems. The technique used for qualitative and rough quantitative determinations of radioactive carbon is very simple. An aliquot of compound containing C^{14} is oxidized to give CO_2, which is converted to $BaCO_3$, whose activity is then determined with a Geiger counter. It is a much more difficult problem, however, to get really accurate quantitative results because of the softness of the C^{14} β-radiation. Although this problem has already been discussed in the literature [1 – 3], we consider it useful to describe a method of working with C^{14} which has justified itself in practice, and in particular, to dwell on those aspects which are stumbling blocks to most beginners in this field.

The method to be described can be divided up into three sections: 1) combustion of an aliquot of the organic material to give CO_2, which is then converted into $BaCO_3$; 2) formation of the solid samples of $BaCO_3$ from the suspension obtained; and 3) measurement of the activity of these formed samples.

Choice of Semple and Combustion. The weight of marked compound required for preparing a test sample is determined on the basis of the following considerations. The thickness of the $BaCO_3$ sample should be roughly equal to the so-called limiting value (ca. 25 mg/cm^2), for reasons given elsewhere in this article. In the case of our samples whose areas were 4.9 cm^2, this amounts to 120 mg of $BaCO_3$. The weight of the sample to be oxidized depends on the number of carbon atoms in its molecule; in the case of $C_{10}H_{10}O_4$, e. g., this should be a minimum of 12 mg.

Combustion was carried out by a rapid combustion method developed in Prof. A. I. Shatenstein's laboratory in the Institute by our colleague L. N. Vasileva. With the author's permission we give the following brief description of the method. A quartz tube 20 mm diameter and 100 cm long was placed in two tubular electric ovens joined to each other end to end. The first oven (through which the gas passes) was heated to 900 – 950°, the part of the tube in that oven being left empty. The second oven was heated to 700 – 750°; the part of the tube in this oven was packed with cupric oxide in the form of short pieces of wire. The inlet of the tube was in the form of a T-piece, the lower end of which (12 mm in diameter) was sealed into the form of a stopper, while the upper branch was in the form of a ground glass socket into which it was possible to fit a tube with a conical joint reaching into the middle of the lower tube. After the oven had reached the requisite temperature, the aliquot of test material, contained in a small quartz tube 12 x 8 mm diameter, was dropped through the socket into the lower tube and the socket closed by means of the tube fitted with a cone, into which was passed a slow (1 – 2 bubbles/second) stream of oxygen freed from CO_2 by passage through two gas scrubbers filled with $Ba(OH)_2$ solution (the criterion used for assessing freedom of oxygen from CO_2 was the complete transparency of the solution in the second scrubber). The lower tube was carefully heated with a blow torch,

gradually moving the flame so that all the test material gradually evaporated and pyrolyzed. Since the flame which formed during pyrolysis of the product was in the form of a "mushroom" with a head of several mm, it was essential to hold the gas torch a little lower all the time. Combustion of the pyrolysis products was completed in the electric oven. This operation was finished by heating the bottom of the lower branch of the T-piece to a light red color for several minutes (total duration of combustion ca. 15 minutes). The CO_2 on emerging from the tube was trapped in 4 – 6 gas scrubbers of the Dreschel type containing 50 ml of a saturated (0.4 N) solution of $Ba(OH)_2$ in each scrubber (that all the CO_2 had been removed from the gas train was checked by observation of the transparency of the last traps). $Ba(OH)_2$ solution absorbs CO_2 just as efficiently as the often recommended NaOH, and in addition acts as an indicator of the way absorption is proceeding.

Forming the Samples. A stainless steel cup with a perforated bottom was used for this purpose (Fig. 1). The cap with two filter papers of " white ribbon" quality 27.3 mm in diameter [1]) fitted into it, was dried to constant weight in a weighing bottle 60 mm diameter, and kept in a desiccator so that the papers did not absorb atmospheric moisture.

Filtration of the $BaCO_3$ suspension through the cup was carried out in a simple apparatus (Fig 2). The cup was fitted into a funnel made of stainless steel and fitted with 3 loops of wire. The gap between cup and funnel was packed with asbestos fiber. The guard ring was removed and a glass cylinder with 3 hooks fitted inside the cup; the front face of the cylinder was ground flat, strictly perpendicular to its axis. Cylinder and funnel were braced together with 3 springs (Fig. 2).

In order that the residual alkali should not absorb atmospheric CO_2, it was transferred into NH_4OH by diluting the suspension in the traps with an equal volume of 0.8 N NH_4Cl which had been made alkaline with ammonia to a pale rose phenolphthalein end point. The suspension, in 10 – 15 ml portions[2]) was transferred into the cylinder of the apparatus (Fig. 2) where the precipitate was allowed to settle and the filtrate sucked off. Any residue adhering to the trap and cylinder was rubbed off with a glass rod fitted with a rubber policeman and washed out with alcohol. The sample was carefully washed 6 – 8 times with water, without breaking up the surface, until there was no reaction for Ba^{2+}; it was then washed 3 times with alcohol. While the suction was still applied the cylinder was held in the hand, the springs removed, and the cylinder carefully removed. The precipitate was left in the cup in the form of an evenly flat disc with a diameter of 25 mm; its edges were somtimes raised a bit and uneven. The guard ring was reinserted in the cup, so that it pressed the filter, thereby not giving it a chance to deform during drying, and also to screen the uneveness in the edges as much as possible. The cup was then dried at 90 – 100° to constant weight (in the weighing bottle), and kept in a desiccator over KOH to prevent exchange with atmospheric CO_2.

1) Made with the aid of steel cutters by hand or on a press. The curvature imparted to the filter paper during pressing must be carefully smoothed out; this was achieved by putting packets of 25 – 50 filter papers soaked in water between two glass plates under a load of ca. 5 kg.

2) Quantitative transfer is not essential.

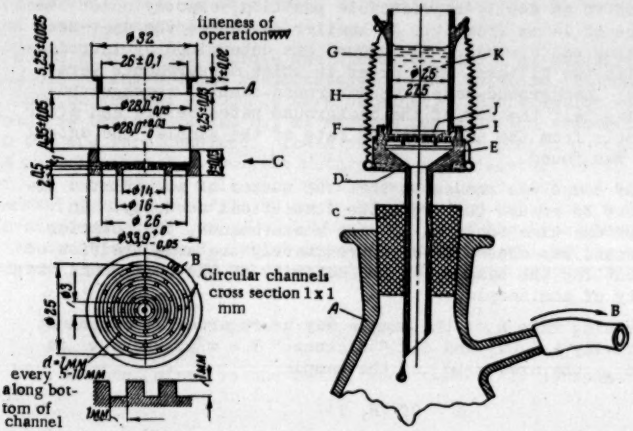

Fig. 1 Cup of stainless steel for forming $BaC^{14}O_3$ samples; A-guard ring; B - numbers, stamped out on the edges, which are the same for cup and ring; C - cup.

Fig. 2 Apparatus for forming samples of $BaCO_3$. A — flask for filtration; B — to vacuum and pump; C-rubber stopper; D-stainless steel funnel; E-compacting ring from asbestos fibers; F-cup; G-glass cylinder with 3 hooks; H-binding springs; I-two filters 27.3 mm diameter; J-$BaCO_3$ precipitate; K-$BaCO_3$ suspension.

Strict observation of all the conditions described above was essential to get smooth precipitates without cracks and other defects, and also to ensure reproducible results. Reproducibility of replicates was ± 2% of the mean. Appearance of cracks, which testified to uneveness in the $BaCO_3$ precipitate and filter, could, as far as we could make out, be ascribed to the following three causes:

1) the precipitate was too thick(> 60 mg/cm^2),

2) poor washing of precipitate free of alkali,

3) substitution of alcohol by acetone and ether.

Measurement of the Activity of Samples. Measurements were carried out with a counter fitted with a mica window 20 mm diameter and a thickness corresponding to 5 mg/cm^2, mounted inside a lead block[1]) and connected with the

[1]) The blocks which we developed were convenient in use but rather complex to prepare. Variants of these blocks in lead and cast are in use in the Karpov Institute. Simpler blocks are being produced on the industrial scale.

usual type of counting set-up. When the cup had been fitted into the holder, it was moved into the side opening of the block right up to the stop. The sample was fixed in an easily reproducible position, exactly under the window at a distance of 14 mm from it. At smaller distances the uneveness of the sample shows up too clearly. Background was determined by introducing an empty cup with two filters. The order in which measurements were made was as follows: background-sample 1-background-sample 2-background-etc.. By subtracting half the sum of the background rates before and after introducing the sample from the net counting rate of the sample, the actual rate of the sample was found.

The duration of count was chosen so that the number of accumulated impulses was sufficient to ensure the requisite statistical accuracy. In order to cut down on the time required to make measurements, the duration of count for background was chosen to be approximately the same fraction of the duration of count for the sample, as the activity of the background was that of the activity of the sample.

The actual counting rate R of the sample may be regarded as dependent only on the net activity A (μCu) and its "thickness" T = w/s, where $\underline{w}$ is the weight (mg) and $\underline{s}$ the area (cm^2) of the sample

$$A = Cf\,(R,\ T) \qquad (1)$$

In so far as the efficiency of the counter was not completely constant, the coefficient C was periodically determined by calibrating the counter against radioactive standards.

Preparation of Standards and Calibration. Strictly speaking, standards for absolute calibration should be made from preparations of $BaC^{14}O_3$ of known activity, but we have no such standards at our disposal. The activity of $BaC^{14}O_3$ is known to change slowly because of exchange with atmospheric carbon dioxide. Such standards would therefore be unstable, while to protect them with some sort of a cover was not feasible because of the softness of the β-radiation. Besides, almost all measurements of the activity of $BaCO_3$ are relative, so that it was sufficient to use standards based on hard β-radiators, for periodic checks on the counter. Absolute measurements were only necessary for preliminary tests, calculation of the experimental conditions, determination of radiation doses etc.; for other determinations it was sufficient to know the absolute activity only approximately (with an error of the order of 20 - 25%). Standards were therefore prepared from fairly old uranyl nitrate $UO_2(NO_3)_2.6H_2O$, in which the uranium had already reached radioactive equilibrium with its decay product, β-active UX_2. The decay rate of U and UX_2 were consequently equal to:

$$\lambda_U N_U = \lambda_{UX_2} N_{UX_2} = -\frac{dN}{dt}\ , \qquad (2)$$

where $\lambda_U = 4.9 \cdot 10^{-18}$ sec^{-1}, while N is the number of atoms of the radio-element. It is easy to calculate from this information that the weight of uranyl nitrate required for a standard of 0.01 μCu (-dN/dt = 370 decays / second) is 0.0632 g.

The standards were prepared as follows. The glass cylinders from the apparatus of Fig, 2 were immersed in molten wax to a depth of 2 - 3 mm, removed after 5 minutes and excess wax removed by touching the cylinder on a bit of warm asbestos. A piece of a filter paper 35 x 35 mm was placed on a smooth rubber sheet, the still warm face of the cylinder was placed on the filter paper, and a 100 g weight placed on the other end. When the wax had cooled and set, the edge of the paper was cut with a razor on a level with the outer surface of the cylinder. True circles were thus prepared which were stuck by 2mm waxed rims to the cylinder face. By putting two

drops of water on the middle of the paper it was checked whether the rim was properly waxed and whether the central part of the paper was free from it. Cylinders thus prepared were dried in a desiccator for 24 hours and then marked with a graphite pencil.

0.632 g of uranyl nitrate was dissolved in a 1 ml standard flask. By taking 0.1 ml and 0.05 ml respectively of this solution, standards equivalent to 0.01 μCu and 0.005 μCu were obtained. This solution was diluted tenfold; by taking 0.2 and 0.1 ml of this new solution standards, of 0.002 and 0.001 μCu were obtained. These aliquots were placed on cylinders prepared as described above and then stored in a desiccator for 48 hours; the paper was cut off the cylinders with a razor, fixed with wax between two circles of washed photographic film 28 mm in diameter and cut along a 27 mm diameter. These standards were then placed in cups, of the type shown in Fig. 1 and the counting rate R_S, which should be proportional to the activity of standard A_S, measured:

$$A_S = C_S R_S \qquad (3)$$

The results (given in the Table) show that C_S is constant within limits of 6%.

Comparison of the Activities of Uranyl Standards

Nominal activity A_S in μCu	Actual counting rate R_S, impulses/minute	$C_S = A_S/R_S$	Deviation from the mean ΔC_S	Ditto in %	Statistical error in counting in %, calculated for 3 minutes
0.01	3177	$3.15 \cdot 10^{-6}$	$0.15 \cdot 10^{-6}$	5.0	1
0.005	1572	3.18	0.18	6.0	1.4
0.002	694	2.89	− 0.11	− 3.7	2.2
0.001 (I)	335	2.99	− 0.01	− 0.3	3.1
0.001 (II)	357	2.81	− 0.19	− 6.3	3.0

Average $3.00 \cdot 10^{-6}$ $\frac{\mu Cu \cdot minute}{impulses}$

A smaller proportion of the hard β-rays of UX_2 is absorbed than of the softer β-rays of C^{14} in the path between sample and the working volume of the counter, so that coefficient C (1) differs from C_S. By comparing the uranium standards with the $BaCO_3$ preparations which we acquired, the absolute activity of which was approximately given in the certificate accompanying them, it was found that $C/C_S = k = 1.46$; the error in this value of k probably amounted to 20%.

Calculation of Self-Absorption and of the Activity of the Preparation. The self-absorption of the hard β-rays of UX_2 can be neglected, but $BaCO_3$ itself strongly absorbs the soft β-rays of C^{14}, a fact which must be taken into account. It is known that for a constant specific activity of samples of $BaCO_3$, the counting rate R measured for them increases with thickness T linearly at first, and then, as a result of self-absorption this rate approximates to a constant limiting rate R_∞ at a limiting ("infinite") thickness T_∞, which is equal to ca. 25 mg/cm² [4] in the case of $BaCO_3$. This relationship can be expressed [5], by the equation

$$G = R/R_\infty = 1 - \epsilon^{-bt}, \qquad (4)$$

while the initial linear rate of growth can be expressed by the equation

$$G_0 = R_0/R_\infty = bT. \qquad (5)$$

Yankwich et al.[4], give $b = 0.283$ mg/cm^2, but it is best to determine $\underline{b}$ empirically for the method of forming the samples (chosen) by plotting log G against T graphically, and determining $\underline{b}$ from the slope.

The initial counting rate $R_0 = R_\infty\, bT = bTR/G$ is a magnitude from which the self-absorption effect is eliminated. It is therefore proportional to the net activity A of the sample, i. e., formula (1) is simplified:

$$A = CR_0. \qquad (6)$$

The specific activity $\underline{a}$ of a sample of $BaCO_3$, taking into account equations (5) and (6) and the relations $\underline{a} = A/w$, $C = 1.46\, C_S$ and $T = w/S$, is shown to be proportional to the limiting counting rate R_∞; this proportionality has been confirmed quite well experimentally [4]:

$$a = \frac{A}{w} = \frac{CR_0}{w} = \frac{1.46 C_S b T}{ST} \cdot \frac{R}{G} = K\frac{R}{G} = KR_\infty. \qquad (7)$$

Coefficient $K = 1.46\, C_S b/S$ can be determined by calibration, which is constant for a given method of sample forming and a given counter sensitivity; in our tests C_S varied from 5.78 to $5.36 \cdot 10^{-6}$ μCu·minutes/impulse, while K, correspondingly, varied from 4.87 to $4.52 \cdot 10^{-7}$ μCu·minutes/mg·impulses.

Thus, determination of activity consists of the following operations; 1) determination of the counting rate R and the thickness T of a test sample; 2) determination of coefficient G for a given thickness T from a graph of function (4), for a given method of sample forming; 3) determination of coefficient C_S by calibrating the counter against standards; 4) calculation of K and determination of $\underline{a}$ according to formula (7). The net activity A of a sample should then be equal to aw μCu, while the molar activity of the $BaCO_3$ will be equal to 197,000 $\underline{a}$ μCu/mol.

In general we found it more convenient to express the activity of marked compounds as molar activities, because the latter does not change during any inessential chemical transformation in which the marked atom maintains its link with the test chemical form, while it is precisely changes in molar activity which indicate the start of attachment of the marked atom to other molecules, i. e., it is possible to decide what happens to the marked atom, the object of any research on the method of marked atoms. It is also necessary to take into account dilution with unmarked products. E. g, during the combustion of $C_{10}H_{10}O_4$ in which one of the carbon atoms is a C^{14}, molar activity decreases to a tenth because of the 9 molecules of unmarked CO_2.

Experimental Error. The most suitable thickness from the point of view of accuracy of results is the range $20 < T < 30$ mg/cm^2, i. e., the range in which T approches T_∞ and where G is ca. 1. For smaller thicknesses the coefficient G starts to deviate appreciably from unity, while it is difficult to determine the correction $1 - G$ with any accuracy better than 10%, as a result of which an appreciable error creeps in. For $T > 30$ mg/cm^2, the sample is rather difficult to form and develops cracks which cannot be tolerated.

By strict observance of all the necessary conditions for forming the samples which have surfaces of good quality, and by calibrating the counter periodically with standards, it is possible to lower the relative experimental errors which arise as a result of the heterogeneity of the samples to 2%. Statistical errors can be reduced further by increasing the number of impulses counted. The absolute errors in the values of the activity depend on the accuracy of the values of K and $\underline{b}$; the differences between the mean values

we accepted for k and b of 1.46 and 0.283 respectively, and the real values may probably amount to ±20%.

The method described can be used for the determination of the activity of solid samples of such soft β-emitters as S^{35}, Ca^{45}, etc., by slight modifications of the methods used for forming smooth, homogenous samples; the technique employed depends on the chemical form in which it is intended to precipitate the test isotopes. This is reflected in the value of the constant used for calculating.

SUMMARY

1.A method is described for the quantitative determination of radioactive carbon C^{14} in organic compounds containing it. The method consists of three stages:

a) rapid combustion of test compound on a micro scale, the CO_2 formed being trapped as $BaCO_3$,

b) formation of $BaCO_3$ samples with homogeneous surface and shape,

c) measurement of the radioactivity of $BaCO_3$ with a Geiger counter.

2) A convenient method is described for the preparation of radioactive uranium standards.

3) A formula is derived by means of which it is possible to determine approximately the absolute radioactivity of $BaCO_3$ samples by comparing them with uranium standards.

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A METHOD FOR THE RATIONAL ANALYSIS OF THE MINERAL COMPONENTS OF BROWN COAL

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A knowledge of the mineral nature of coal is of considerable interest both for research workers developing methods for the complex use of coal, and also for workers studying the enrichment of coal, in solving questions on the choice of a rational method of enrichment. Moreover, data on the mineral composition of the inorganic contaminants of coal can, to a certain extent, serve as a guide to how coal or coal strata have been formed.

Sufficiently reliable results can be obtained by combining two methods, which supplement and control each other; viz., qualitative determination of the macro- and micro- structure of coal and its inclusions; and a semi-quantitative rational analysis of its mineral components.

Nevertheless it is only the petrographic method of studying coal which has been studied to any considerable extent and described in the literature, and this has limited application from the point of view of determining the mineral composition of coal.

In order to fill this gap, we set out to develop in detail a method for the rational analysis of the mineral composition of coal, and selected as our test material brown coal containing little ash and large amounts of ash, respectively, as well as a considerable amount of humic acid derivatives.

According to Zhemchuzhnikova [1], and other coal petrographers [2], coal may contain any of the following minerals: epsomite, gypsum, serpentine, hetite or limonite, galluasite, etc (which dissolve or break up in hydrochloric acid), and minerals of the rutile, kaolin, and chlorite groups, and also quartz, pyrite, and traces of zircon, etc. (practically insoluble in hydrochloric acid).

It is also known that the mineral components of coal can be divided into external and internal components. By external minerals are meant those which were introduced mechanically into the coal seam during its formation. These materials are usually insoluble in hydrochloric acid; any conclusions re these materials can only be obtained indirectly on the basis of the results of chemical analyses of brown coal ash.

Internal minerals, on the other hand, are those which formed parts of the plant material from which the coal itself was formed; in some cases however, the inorganic material of the internal minerals may not have been derived from the mineral materials of the plants. E. g., the humates of calcium and iron are reaction products of inorganic material with organic material formed as the result of secondary processes, and present in brown coal.

Internal minerals, as a rule, dissolve either in water or in hydrochloric acid, while some of them are partly soluble in water and partly soluble in acid.

Taking all facts into account, one can to a first approximation, get

a qualitative or semi-quantitative idea of the minerals comprising brown coal from a given locality by using a method based on a rational analysis of its mineral composition after preliminary determination of the macro- and micro- structure of the strata surrounding the coal.

For this purpose the chemical composition of brown coal ash and also of the water and hydrochloric acid extracts of the test coal are determined. Afterwards (by combining these results) it is calculated what minerals compose a given coal, and the approximate component of each in the coal.

A study of the chemical composition of brown coal ash is also of considerable practical interest for working out the best way of using it in industry and in the national economy, and for determining its fusibility, etc..

Ashing of Brown Coal and Determination of the Chemical Composition of the Ash

Our experience in determining the ash of young brown coal showed that considerable variations were observed in the ash content and also in the chemical composition of the ash, according to the method used for ashing, particularly when the sulfurous acid method was used. The latter fact is clearly illustrated by the results adduced in Table 1.

TABLE 1

Comparison of Ash Composition Obtained by Various Ashing Methods

Test material	Ashing method	Chemical composition of the ash in %							Total
		SiO_2	Al_2O_3	F_2O_3	TiO_2	CaO	MgO	SO_3	
4865	Slow	57.83	15.92	2.25	2.00	7.49	3.63	10.70	99.82
4865	Rapid	60.13	16.56	2.36	2 10	7.80	3.78	7.31	100.04
8395	Slow	29.39	25.48	5.58	0.77	14.16	2.92	22.04	100.24
8395	Rapid	32.41	28.02	5.99	0.81	15.52	3.22	13.98	99.95

The results given in Table 1 show that the percentage contents of the ash components change with the amount of sulfur left in the ash, according to the ashing conditions of the brown coal.

When brown coal is rapidly ashed in a muffle preheated to 800° ± 25°, all the organic sulfur and part of the pyrites sulfur leave the zone of the ashed coal as sulfur dioxide. It follows from this that in order to come to any conclusions re the chemical composition of brown coal ash which is insoluble in hydrochloric acid, it is essential: 1) to ash the coal quickly, not slowly; 2) to determine the percentage pyrites sulfur in an average sample of this coal.

The ash for chemical analysis was usually prepared as follows: 15 – 20 g of brown coal, depending on the ash content, was ashed rapidly (in an oven preheated to 800 ± 25°). The ash was analyzed by a method described in Stadnikov's monograph [3]. The percentage of pyrites sulfur was determined previously or at the same time on another sample of the same material by means of a generally accepted method, while the approximate contents of the rare elements were determined on another sample of ash spectrographically.

Preparation and Analysis of Water Extracts

50 – 100 g of the air dried coal was poured into a flask with five times its amount of distilled water and the whole shaken for 3 minutes. The contents of the flask were then transferred to a funnel and filtered. Moisture content of the test coal was determined simultaneously according to All Union State Standard (GOST) 147-41 or 6383-52.

TABLE 2

Approximate Composition of the Mineral Part of Low Ash Brown Coal According to the Results of Chemical Analysis of the Ash, and of the Water, and Hydrochloric Extracts Respectively

Components	Water extracts	In % on the dry coal: Hydrochloric acid extract	Residue insoluble in hydrochloric acid	Chemical composition of ash	Chemical composition of ash in % on the dry ash
SiO_2	–	0.04	8.36	8.40	56.40
Al_2O_3	–	0.92	0.25	1.17	7.84
Fe_2O_3	–	0.54	0.44	0.98	6.56
TiO_2	–	–	0.41	0.41	2.76
CaO	0.02	2.84	–	2.87	19.20
MgO	0.01	0.43	–	0.44	2.95
SO_3	0.04	0.11	0.55	0.70	4.67
CO_2	–	1.60	–	–	–
	0.07	6.48	10.01	14.97	100.38

Minerals	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	SO_3 (%)	H_2O (%)
Soluble or Break Down in Hydrochloric Acid								
Epsomite...	–	–	–	–	–	0.01	0.02	–
Gypsum....	–	–	–	–	0.09	–	0.13	0.06
Calcite....	–	–	–	–	2.04	–	–	–
Serpentine.	0.43	–	–	–	–	0.43	–	0.14
Galluasite.	1.10	0.92	–	–	–	–	–	0.52
Limonite...	–	–	0.54[1]	–	–	–	–	0.08
Calcium humate....	–	–	–	–	0.73	–	–	–
Practically Insoluble in Hydrochloric Acid								
Pyrites....	–	–	0.44	–	–	–	0.85	–
Rutile group.....	–	–	–	0.41	–	–	–	–
Kaolinite..	0.30	0.25	–	–	–	–	–	0.10
Quartz group.....	6.57	–	–	–	–	–	–	–
Total.....	8.40	1.17	0.98	0.41	2.86	0.44	1.00	0.9

1) Some of the Fe^{3+} may be present as iron humate

Notes. 1) The best coal had an ash of 14.97%. 2) The % of pyrites sulfur in the coal was 0.35. 3) Traces of zirconium and other rare elements were detected spectrographically.

TABLE 3

Approximate Composition of the Mineral Part of High Ash Brown Coal According to the Results of Chemical Analysis of the Ash and of the Water and Hydrochloric Acid Extracts Respectively

Components	In % on the dry coal			Chemical composition of ash in % on the dry ash
	Water extracts	Hydrochloric acid extract	Residue insoluble in hydrochloric acid	Chemical composition of ash	
SiO_2	–	0.10	26.75	26.85	68.63
Al_2O_3	–	1.39	4.54	5.93	15.25
Fe_2O_3	–	0.21	0.99	1.20	3.06
TiO_2	–	–	0.96	0.96	2.44
CaO	0.06	2.06	0.49	2.61	6.68
MgO	0.03	0.34	0.20	0.57	1.47
SO_3	0.15	0.13	0.85	1.13	2.90
ε	0.24	5.33	34.78	39.25	100.43
CO_2	–	1.10	–	–	–

Minerals	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	SO_3 (%)	H_2O (%)
Soluble or Break Down in Hydrochloric Acid								
Epsomite..	–	–	–	–	–	0.03	0.06	0.10
Gypsum....	–	–	–	–	0.15	–	0.23	0.10
Calcite...	–	–	–	–	1.40	–	–	–
Serpentine	0.34	–	–	–	–	0.34	–	0.10
Galluasite	–	–	0.21[1]	–	–	–	–	0.03
Limonite..	1.66	1.39	–	–	–	–	–	0.54
Calcium humate...	–	–	–	–	0.57	–	–	–
Practically Insoluble in Hydrochloric Acid								
Pyrites...	–	–	0.59	–	–	–	1.25	–
Rutile group....	–	–	–	0.26	–	–	–	–
Titanite (sphene group)...	1.05	–	–	0.70	0.49	–	–	–
Kaolinite.	5.16	4.29	–	–	–	–	–	1.50
Prochlorite.....	0.25	0.30	0.40	–	–	0.20	–	0.10
Quartz....	18.34	–	–	–	–	–	–	–
Total...	26.80	5.98	1.20	0.96	2.61	0.57	1.54	2.47

1) Some of the Fe^{3+} may be present as iron humate

Notes. The test coal had an ash of 39.25%: 2) the % of pyrites sulfur in the coal was 0.50; 3) traces of zirconium, nickel, vanadium and other rare elements were detected spectrographically.

The percentage of CaO, MgO, SO_3 and Cl, and in some cases, total alkali, were determined by the usual analytical methods in the water extract.

The analytical results were calculated on the basis of the dry weight of coal.

Preparation and Analysis of Hydrochloric Acid Extracts

50 g of air-dried coal was poured into a flask with five times its amount of 10% hydrochloric acid. The contents of the flask were boiled for 1 hour and then filtered and the residue washed with water until the appearance of colloids.

SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and SO_3 were determined in the filtrate by the usual methods. Simultaneously, the moisture content of the coal was determined according to GOST - 147-41 or 6383-52 and carbonate content determined volumetrically from the carbon dioxide released [4].

Analytical results were calculated on the basis of the dry weight of coal.

Methods of Calculating the Results for the Rational Method of Analyzing the Mineral Components of Coal

The method used for calculating the composition of the mineral part of brown coal by combining results characterizing the percentage contents of the components in the water and hydrochloric acid extracts, and in the ash, is illustrated by the examples given in Tables 2 and 3.

The magnesium oxide in the aqueous extract may be found in the mineral part of the coal in the form of epsomite, while the magnesium oxide in the hydrochloric acid extracts may be found in the coal in the form of serpentine; finally, the magnesium oxide insoluble in hydrochloric acid may be a component of chlorites.

CaO in the aqueous extract and part of the CaO in the hydrochloric acid extract is found in the mineral part as gypsum, while the rest of the CaO in the hydrochloric acid enters into the composition of calcite and calcium humates. Finally the CaO in the ash insoluble in hydrochloric acid forms part of titanite.

Ferric oxide soluble in hydrochloric acid may have been present as limonite, hetite or iron humate. The iron oxide in the ash insoluble in hydrochloric acid was formed as the result of combustion of pyrites and decomposition of minerals of the chlorite group. Al_2O_3 is a component of minerals of the kaolin group which break down but do not dissolve in hydrochloric acid. TiO_2 is present in minerals of the rutile group or the sphene group, e. g., titanite. Finally SiO_2 enters into the composition of minerals which break down or are insoluble in hydrochloric acid. SiO_2 is present to a considerable extent as quartz.

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BRIEF COMMUNICATIONS

IN SITU METHOD OF DETERMINING MANGANESE IN GLASS

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The method usually adopted for producing glass with a violet color is incorporation of manganese oxide (0.1 – 20%); sometimes, ferric oxide and nickel oxide are also added.

In order to analyze the glass for its manganese oxide content during manufacture and when it is finished we used an in situ method [1], which requires 15 – 20 minutes to carry out.

The glass is brought into solution without taking aliquots; the solutions formed are determined colorimetrically in 10-ml glass measuring cylinders after oxidation of divalent manganese to MnO_4 by ammonium persulfate in the presence of silver. All operations are carried out in the 10-ml glass cylinders. Evaporation of the solution to dryness in platinum crucibles is not permissible, since the fluoride ion not only does not interfere with the reaction, but actually stabilizes the trivalent manganese [2], formed during the reaction.

Analytical Procedure. Small areas of the cleaned surfaces of test and standard glass are isolated by means of paraffin wax, and into the little craters formed are placed two drops of hydrogen fluoride which are kept in contact with the glass surfaces for 5 minutes; the drops are constantly stirred with glass rods covered with paraffin wax. When reaction is complete the solutions in the little craters are diluted with 3 – 4 drops of water and the whole transferred into ordinary 10-ml measuring cylinders with the aid of glass capillaries. Craters and cylinder walls are washed with water and the volume made up to 1.5 – 2 ml; 3 – 4 drops of sulfuric acid (1:1) are then added and the solutions boiled for a few seconds till the solutions clarify (boiling is carried out while the cylinders are rotated, the surface being heated a little higher than the base – 0.6 - 1 cm). 1 – 2 ml lots of water are then added to the cylinders, followed by the requisite reagents (0.5 ml saturated ammonium persulfate, 2 – 3 drops of 0.1% silver nitrate, and 4 – 6 drops of sulfuric acid – 1:3), and the cylinders heated again until the appearance of a raspberry color. The colors of the standard and test solutions are matched by adding water to the more intensely colored one. When the manganese content of the glass is high, colorimetric determination is carried out in a second (sometimes in a third) cylinder. In such cases, the solution in the first cylinder is diluted with water to 10 ml, a definite number of ml (0.5, 1, 2 ml) transferred to the second cylinder, and the corresponding reagents added.

The manganese content is calculated from the equation:

$$C_{t.s} = \frac{V_{t.s}}{V_{s.s}} C_{s.s}$$

Here $C_{t.s}$ and $C_{s.s}$ – are the manganese contents (in %) in the test and standard samples; $V_{t.s}$ and $V_{s.s}$ – the volumes of test and standard solutions for equal color intensities.

This method developed for manganese content was checked on the FEK (M) photocolorimeter. In this case, the colored solutions in the respective cylinders were diluted to the same volume, mixed, and transferred to clean cells.

Optical density was measured with a green filter. The manganese content (in %) was calculated by means of the formula:

$$C_{t.s.} = \frac{D_{t.s.}}{D_{s.s}} C_{s.s}$$

Here $D_{t.s}$ and $D_{s.s}$ – are the optical densities of the test and standard solutions.

The mean values obtained for manganese contents determined by this method are given in the table.

Determination of Manganese in Glass

Sample number	Mn_2O_3 obtained in %			
	Determined volumetrically	Determined by the in situ method	Difference	Photocolorimetric finish of the in situ method
10	1.70	1.73	+ 0.03	1.72
20	1.15	1.14	− 0.01	1.12
460	0.70	0.73	+ 0.02	0.72
Dyatkovsky factory analysis	Gravimetric method 8.63	8.62	− 0.01	

As the data of this table testify, determination of manganese by the in situ method is completely satisfactory.

This method is already in use in a Leningrad factory producing artistic glass and glass of other types, and in the Dyatkovsky crystal factory and the "Neman" factory.

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THE USE OF CHLORAMINES IN QUALITATIVE ANALYSIS

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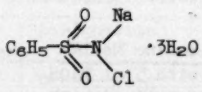
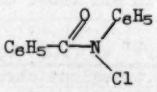
In recent years use has been made in analytical chemistry of chloro-organic compounds called chloramines, of which the following are examples:

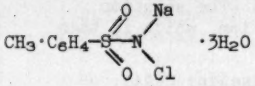
Chloramine B



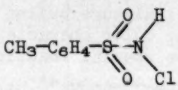
Chloramine VNITI-2



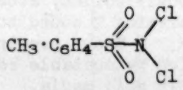
Geiden's chloramine

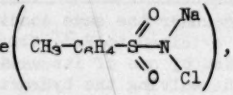


Chloramine T



Dichloramine T



The one most often used is chloramine T as the sodium salt of p-toluenesulfochloramine  , mainly because of its good solubility in water. The other chloramines noted above are either practically insoluble or only sparingly soluble in water.

Chloramine T is mainly used in volumetric analysis for the determination of various materials [1], and in qualitative analysis as a substitute for chlorine water and for a number of colorimetric reactions for organic materials.

Chloramine T solutions are stable over long periods when kept in dark glass containers.

Chloramine in acid solution can be used satisfactorily instead of chlorine or bromine water for oxidizing trivalent chromium to the sexivalent state. This reaction is used in qualitative analysis at the present time [2].

In view of the increasing use of chloramine T in analytical chemistry, we thought it expedient to study chloramine T from the point of view of its use as an oxidizing agent in qualitative analysis. Our studies showed that it is possible to oxidize Mn^{2+} and Fe^{2+} to Mn^{IV} and Fe^{III}, respectively, with chloramine T in alkaline media, and also for bringing nickel and cobalt sulfides into solution [3].

The mechanism of the oxidation of Cr^{IV}, Mn^{2+} and Fe^{2+} in alkaline media is still not clear. Probably, the oxidation process is connected with the hydrolysis of chloramine T with formation of: $CH_3 \cdot C_6H_5 \cdot SO_2 \cdot NH_2$, NaOCl and NaOH: hypochlorous acid and its sodium salt oxidize Cr^{III}, Mn^{2+}, Fe^{2+}. Oxidation in alkaline media apparently proceeds as follows:

$$2\ Cr^{3+} + 10\ \overline{OH} + 3\ OCl^- = 2\ CrO_4^{2-} + 3\ Cl^- + 5\ H_2O$$

$$Mn^{2+} + 2\ OH^- + OCl^- = MnO(OH)_2 + Cl^-$$

$$2\ Fe^{2+} + 4\ OH^- + H_2O + OCl^- = 2\ Fe(OH)_3 + Cl^-$$

The possibility of the decomposition of chloramine T in alkaline media to form active chlorine, which then reacts directly with Fe^{2+} ions, is not excluded.

The experiments described below demonstrate the possibility of using chloramine T solutions in all those cases where chlorine water is used in qualitative analysis.

1. Oxidation of Cr^{3+} to CrO_4^{2-} by Chloramine T in Alkaline Media. 1 ml of a solution of a trivalent chromium salt is mixed with 5 ml NaOH (10%); the solution is evaporated to a small volume and then mixed with 2 ml of 10% NaOH. 1 – 2 grains of chloramine T are added to the solution obtained and the final mixture boiled for 3 – 5 minutes. The solution thereupon acquires the color characteristic of the CrO_4^{2-} ion, which is then detected by one of the special reactions for this ion.

2. Oxidation of Mn^{2+} to Mn^{4+} by Chloramine T in Alkaline Media. 1 ml of a solution of a divalent manganese salt is mixed with 3 ml of 5% NaOH solution and the mixture vigorously boiled, after which another 1 ml of NaOH is added and 1 grain of chloramine T added to the mixture obtained. This mixture is boiled for 2 minutes. A brown precipitate of $Mn(OH)_2$ is formed in which Mn^{IV} can be identified by suitable reactions. This reaction may be carried out even in weakly acid media.

3. Oxidation of Fe^{2+} to Fe^{3+} by Chloramine T in Alkaline Media. Oxidation of Fe^{2+} to Fe^{3+} is effected under the same conditions as used for the oxidation of Mn^{2+}. The Fe^{2+} oxidized to Fe^{3+} thereupon precipitates as the hydroxide. The iron is detected by one of its usual characteristic reactions [NH_4SCN, $K_4Fe(CN)_6$] after dissolving the hydroxide in hydrochloric acid.

4. Effect of Chloramine T on the Sulfides of Ni and Co. To the precipitate of NiS or CoS (taken on a knife point) is added, in the cold, a solution of HCl, followed by 2 – 3 ml of a saturated solution of chloramine T. The mixture is heated to the boil for 2 – 3 minutes; when this is done the usual separation of sulfur is observed. The solution is filtered free of sulfur, and split into two parts, in which Ni^{2+} and Co^{2+} are identified by the usual characteristic reactions.

Similar results were obtained when the reaction was carried out in a neutral medium.

Received January 13, 1954

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MIXED ONE-COLOR ACID-BASE INDICATOR

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Mixed acid-base indicators have found wide application in analytical chemistry [1, 2]. Hitherto, however, no mixed indicators composed of one color acid-base indicators have been described in the literature. The use

Table of One-Colored Acid-Base Indicators

Test number	Designation	pH limits	Color change
1	Picric acid	0.0 – 1.3	Colorless-yellow
2	Quinaldinic red	1.0 – 2.0	Colorless-red
3	Pentamethoxyred	1.2 – 3.2	Red violet-colorless
4	Dinitrophenol-β	2.4 – 4.0	Colorless-yellow
5	Hexamethoxyred	2.6 – 4.6	Red rose-colorless
6	Dinitrophenol-α	2.6 – 4.6	Colorless-yellow
7	Red-violet 5PC	3.6 – 6.0	Rose – colorless
8	Dinitrophenol-γ	4.0 – 5.8	Colorless-yellow
9	Water blue	4.7 – 7.0	Blue-colorless
10	Heptamethoxyred	5.0 – 7.0	Red-colorless
11	Nitrophenol-ortho	5.0 – 7.0	Colorless-yellow
12	Nitrophenol-para	5.6 – 7.0	Colorless-yellow
13	Pinachrome	5.6 – 8.0	Weak rose-red violet
14	Dinitrobenzoyleneurea	6.8 – 8.0	Colorless-yellow
15	Nitrophenol-meta	6.8 – 8.6	Colorless-yellow
16	Quinoline blue	7.0 – 8.0	Colorless-violet
17	1,3-Bis(3-methyl-4 nitro-5-pyrozolyl) triazene	7.0 – 8.5	Colorless-orange
18	Naphtholphthalein-α	7.4 – 8.6	Colorless-green blue
19	Ethyl-bis(2,4-dinitrophenyl) acetate	7.5 – 9.1	Colorless-blue
20	Phenolphthalein	8.2 – 10.0	Colorless-red
21	Cresolphthalein-ortho	8.2 – 9.8	Colorless-red
22	Xylenolphthalein-para	8.9 – 10.2	Colorless-blue
23	Thymolphthalein	9.3 – 10.2	Colorless-blue
24	Alizarin yellow ZhZh	10.0 – 12.1	Weak yellow- yellow brown
25	Nitramine	11.0 – 12.5	Colorless-red brown
26	Malachite green	11.0 – 13.5	Green-colorless
27	1,3,5-Trinitrobenzene	11.5 – 14.0	Colorless-orange

of mixed one color acid-base indicators permits one to get a colorless interval in various pH ranges. Thus, we prepared a mixed indicator from hexamethoxyred (hexamethoxytriphenylcarbinol) and thymolphthalein by mixing equal volumes of 0.1% alcoholic solutions of these indicators.

At present about 40 one-color acid-base indicators are known [3 – 6]. These include nitrophenols, dinitrophenols, trinitro compounds, nitramines, ethyl-bis(2,4-dinitrophenyl) acetate, phthaleins (phenolphthalein, thymol-

phthalein etc), penta-, hexa-, and hepta- methoxytriphenylcarbinols, quinoline blue, quinaldine red, pinachrome, water blue, red violet 5 PC, malachite green, etc..

The mixed indicator changed color in the following pH ranges:

$$0 \underset{\text{Red}}{\longleftrightarrow} 4.6 \underset{\text{Colorless}}{\longleftrightarrow} 9.3 \underset{\text{Blue}}{\longleftrightarrow} 14$$

By selecting suitable one-color acid-base indicators which are colored in acid media, e. g., Nos. 3, 5, 7, 9, and 10, and mixing them with ones which are colored in alkali, e. g., Nos. 16 – 23, it is possible to get mixed indicators with a colorless interval in the neutral region of the pH scale. E. g., a mixed indicator made from red violet 5PC and quinoline blue should exhibit, according to published results [1], the following color changes on changing the pH:

$$\underset{\text{Rose}}{\longrightarrow} 6.0 \underset{\text{Colorless}}{\longleftrightarrow} 8.0 \underset{\text{Violet}}{\longleftarrow}$$

Received July 17, 1954

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REVIEWS

Analysis of the Metals. Published by Chemikerausschuss der Gesellschaft Deutscher Metallhuten- und Bergleute e. V. Dr. O. Proske, director, Prof. Dr. H. Blumenthal and Dr. F. Ensslin. 2nd Vol. Industrial Analyses (Betriebsanalysen). First Part XI + 716. 2nd Part IV + 706. Springer-Verlag. Berlin, Gottingen, Heidelberg, 1953.

It is generally known that study of advanced work in other countries is of great importance in the field of production control. The second volume (in two parts) of " The Analysis of Metals " published in 1953 permits one to get a complete picture of the state of technical analysis in the German metallurgical industry [1]. 100 analytical chemists participated in choosing and checking the analytical methods. The work therefore includes a vast amount of practical knowledge and experience.

The first 45 chapters are devoted to a description of the methods of determining individual elements and methods of analytical control during production. After a short resume of information re the natural sources of a metal and some of the methods used for its determination, the most important gravimetric, volumetric, colorimetric, polarographic and other methods of determining the metal are given in detail, as well as methods for analyzing the original raw materials, for analysis of the metal during its production, for intermediate and final products, for its alloys, metal oxides, salts, and other materials. Considerable attention is devoted to methods for determining contaminants in the pure metals.

The principle of each method is indicated as well as its scope, its accuracy, time to carry it out, source of errors and possible ways of eliminating these errors; a short bibliography is also included. Alongside description of the most modern methods and the use of physico-chemical apparatus, considerable space is devoted to classical methods, including some methods worked out recently, which can be used in factory laboratories which are not so well equipped as others. Chemical control of the production of all metals which are important in practice is considered in detail.

Separate chapters are devoted to analytical methods for metallic and non-metallic coatings, determination of oxygen in metals, analysis of fire resistant materials, fuel, sewage and boiler water.

The principles and potential used of photometric, polarographic, potentiometric, and spectrochemical methods of analysis are clearly set out in special chapters, and a brief description of the requisite apparatus given, numerous spectrochemical methods of analysis of many metals and alloys are included, as well as flame photometric methods of determining the alkali and alkaline-earth metals.

Separate chapters are devoted to descriptions of the preparation of standard solutions, indicators, and various reagents, and to German standards for aluminum, lead, copper, magnesium, nickel, silver, gold, platinum, zinc,

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[1]) The first volume, published in 1949, contained information on accepted arbitrary methods.

tin, and their alloys.

It is difficult to think of any other book in current world literature which contains such a wealth of material as the book under review. This book is of undoubted interest to a wide circle of Soviet analytical chemists working in laboratory factories, scientific-research laboratories, and also in educational institutes.

All the same, in our opinion, some of the analytical methods which are recommended, particularly for less common elements, require further study and improvement. E. g., separation of traces of indium from zinc ores and intermediate products by Blumenthal's method (Part I,p. 344 et seq,), which does not always give reliable results. Some new methods which have justified themselves are absent. E. g., in the chapter on bismuth (Part 2, p. 120 et seq.) the determination of this metal in the presence of lead and other elements by titration with disodium ethylenediaminetetracetate (Complexone III), published in 1951, is not included.

The number of such examples can be multiplied; all the same this fact does not lower the overall high value of this book.

" The Analysis of Metals " is a good reference book for a wide circle of analytical chemists. The book will undoubtedly be of considerable interest to Soviet readers when it is translated into Russian.

A. I. Busev and N. G. Polyansky

CHRONICLE

Fedor Mikhailovich Shemyakin

On His 50th Birthday and His 25th Year of Teaching Activity

Professor Fedor Mikhailovich Shemyakin, Doctor of Chemical Sciences celebrated his 50th birthday in January 1955.

His scientific work began in 1926, in which year, while still a student on the chemical faculty of Moscow State University, he published a number of scientific papers.

Having finished at Moscow University in 1930, Shemyakin was made an assistant in the same year, and then in 1933 he was made a lecturer at the same university where he worked until 1937. During this period he lectured on analytical chemistry and gave a course on colloid chemistry in Moscow Textile Institute.

For his research on the classification of chemical compounds and his improvements on physico-chemical methods of analysis he was awarded the degree of Candidate of Chemical Sciences by the USSR Academy of Sciences. From 1934 – 1938 Shemyakin carried out work for his doctorate under N. S. Kurnakov in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, and successfully defended his thesis for his doctorate on the theme of " Physico-Chemical Periodic Processes ".

His work is of great importance in chemical literature. His monograph on physico-chemical processes written in collaboration with P. F. Mikhalev was published in 1938. Up to the present, apart from 150 published papers he also has 15 author's certificates on questions relating to colorimetric determination of rare elements, the use of new organic reagents, and chromatographic methods of analysis.

Half of all his published work relates to the solution of various problems in analytical chemistry.

As long ago as 1935 Shemyakin adopted the method of physico-chemical analysis as a basis for accurate methods of chemico-analytical gravimetric and colorimetric determinations.

Shemyakin has shown that by using ammonium benzoate or ammonium cinnamate it is possible to separate quadrivalent vanadium from the divalent cation which hydrolyzes with greater difficulty.

Thus, among his scientific activities one should note his work on the study of periodic processes, on the classification of special relationships which occur in the periodic system (the shift law), and his work on analytical chemistry.

Of special importance in his analytical work are his studies on the colorimetric determination of rare elements. Apart from direct studies in colorimetry, Shemyakin has contributed to the wider use of this method, and has translated in collaboration with A. E. Uspensky the book " Photometric Analysis " by R. Joy.

Shemyakin has described new qualitative reactions as well as colorimetric and potentiometric methods of determining cerium, lanthanum, and

thorium. In 1938 he proposed a very specific reaction for cerium with anthranilic acid.

Much of his work has consisted of developing the use of organic reagents in analytical chemistry. He was one of the first to continue the research of M. I. Ilinsky on α-nitroso-β-naphthol, and used it for determination of vanadates and molybdates.

Shemyakin heads the Dept. of Analytical Chemistry in the Moscow Pharmaceutical Institute, where he continued to develop new lines in analytical chemistry, using pharmaceutical preparations for the determination of the most important elements.

As long ago as 1937 he published a number of papers on reactions of the rare-earths and related elements with alkaloids; in particular, with morphine.

His studies in chromatography are particularly wide. Shemyakin adapted physico-chemical analysis in the field of chromatographic adsorption to a study of the kinetics of development of chromatographic bands on columns of aluminum oxide, permutite, and various organic adsorbents (reported at the second conference on Physico-Chemical Analysis in 1949).

F. M. Shemyakin, together with T. B. Gapon and E. N. Gapon, got ion exchange chromatograms on permutite and showed that ion-exchange is one of the variants of chromatographic analysis.

Many scientific research projects and theses have been carried out under Shemyakin's guidance since 1933.

At present Shemyakin is the Chairman of the Permanently Acting Section on the Application of Chromatography of the USSR Academy of Sciences Chromatography Commission.

Shemyakin always finds time to give scientific lectures before a wide audience, and also to organize student scientific work; he is a scientific leader of the NSO of Moscow Pharmaceutical Institute.

We wish Shemyakin good health, many years of life, and new successes for the good of our great socialist country.

Yu. Klyachko

M. Tarasenko

A. Brusntsev